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Tribological Properties of Metal-Matrix Composite Materials Reinforced by Superelastic Hard Carbon Particles

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Abstract—Metal-matrix composite materials (CMs) are synthesized from a mixture of a metal powder (Ti, Fe, Co, Ni, Cu, Al-based alloy) and fullerenes (10 wt %). The thermobaric synthesis conditions (700–1000°C, 5–8 GPa) ensure the collapse of fullerene molecules and their transformation into superelastic carbon phase particles with an indentation hardness H_{IT} = 10–37 GPa, an elastic modulus E_{IT} = 60–260 GPa, and an elastic recovery of >80% upon indentation. After reinforcing by superelastic hard carbon, the friction coefficient of CM decreases by a factor of 2–4 as compared to the friction coefficient of the matrix metal, and the abrasive wear resistance increases by a factor of 4–200. Superelastic hard carbon particles are a unique reinforcing material for an increase in the wear resistance and a simultaneous decrease in the friction coefficient of CM.

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INTRODUCTION

According to the results of studying the antifriction and wear-resistant properties of the materials intended for friction pairs [1–3], these properties can be significantly improved when carbon diamond-like coatings (DLCs) are applied. Such coatings ensure a decrease in the friction coefficient, a high wear resistance, low adhesion to the counterbody material, and chemical inertness. The substantial disadvantages of DLCs are related to the exfoliation of a coating from the substrate and the impossibility of using the electrical conductivity and the thermal conductivity of a metallic matrix. At present, the products of the pressure-induced transformation of fullerenes are bulk materials, the structure and properties of which are similar to those of diamond-like coatings [4, 5]. The structure of such materials consists of bent graphene planes, which are connected to each other by covalent bonds to form a three-dimensional cage [4]. These high-strength bonds prevent a shift of graphene planes, which provides a high strength of the material and its high elasticity due to the ability of these planes to bend and to restore their shape. Hard and elastic materials with a high ratio of the microhardness to the elastic modulus (H_{IT}/E_{IT}) are thought to be the most effective materials for increasing the wear resistance and improving the tribological characteristics [6]. An increase in ratio H_{IT}/E_{IT} favors the accommodation of surface deformation and the absorption of shock loads without fracture. Ratio H_{IT}/E_{IT} determines the degree of elastic recovery upon indentation. The materials with $H_{IT}/E_{IT} > 0.15$ are considered as ideally elastic materials [7]. The action of high pressures and temperatures on a mixture of metal and fullerene powders ensures the collapse of fullerene molecules and their transformation into an atomic superelastic hard carbon phase during simultaneous compacting of the powders into a composite material (CM) [8–10].

The purpose of this work is to study the abrasive wear resistance and the tribological properties of CMs reinforced by superelastic hard carbon in order to design new antifriction metal-matrix materials.

EXPERIMENTAL

The metallic matrix was made of the following metal powders with various carbide-forming abilities: nickel (99.85% Ni, average granule size of 25 μm), cobalt (99.98% Co, average granule size of 12 μm), iron (99.98% Fe, average granule size of 60 μm), titanium (99.5% Ti, average granule size of 85 μm), aluminum-based alloy (AK12M2MgN alloy, average granule size of 150 μm), and inactive copper powder weakly dissolving carbon in the solid state (0.03% C are dissolved at 800°C) [11]. CM samples 5–10 mm in diameter and 2–5 mm in height were synthesized from a mixture of 90 wt % metal powder and 10 wt % $C_{60/70}$ fullerene mixture in a hydraulic press in lens- and

Table 1. CM synthesis pressure p and temperature t and the following properties of the reinforcing carbon phase: microhardness H_{IT}, elastic modulus E_{IT}, degree of elastic recovery R, and ratios H_{IT}/E_{IT} and H_{IT}^2/E_{IT}

CM matrix	p, GPa	t, °C	H_{IT}, GPa	E_{IT}, GPa	R, %	H_{IT}/E_{IT}	H_{IT}^2/E_{IT}
AK12M2MgN	5	650	10	61	93	0.16	1.6
Ti	5	1000	14	73	96	0.19	2.7
Fe	5	900	15	79	94	0.19	2.8
Cu	8	800	31	214	83	0.14	4.5
Ni	8	800	35	263	79	0.13	4.7
Co	8	800	37	246	84	0.15	5.6

toroid-type cells under a high hydrostatic pressure [12]. The charges for CMs were mechanically mixed for 5 min, and fullerites were mechanically activated in Frich mill for 4 min in some cases (for CMs based on copper, nickel, and cobalt).

The microstructure of the synthesized CMs was analyzed with Reichert and Olympus GX51 optical microscopes. The phase composition of the CMs was studied by X-ray diffraction (XRD) on an Ultima 4 (Rigaku) diffractometer using Cu$K\alpha$ radiation, a high-speed D/teX detector, the PDXL software package, and the PDF-2 database.

The carbon phases formed from fullerites were identified by Raman spectroscopy. Raman spectra were recorded on a high-resolution CRM 200 (WITec) spectrometer equipped with a confocal attachment (10-mW laser with a wavelength of 532 nm). The laser spot size in the focus was ~1 μm.

Indentation microhardness H_{IT} of carbon phases was measured according to State Standard GOST R 8.748–2011 [13] using a multifunctional Universal Tester UMT-3MO (CETR) testing device to record loading–unloading curves at a load of 0.5 N.

Tribological tests of CM samples were carried out on the multifunctional Universal Tester UMT-3MO (CETR) device. These tests were carried out using the pin-on-disk scheme during circular motion at a linear velocity of 0.3 m/s for 2 h on a counterbody made of steel with hardness 62 *HRC* at a normal load of 50 N for the CMs based on cobalt, iron, nickel, and titanium and a load of 10 N for the CMs based on copper, nickel, and aluminum-based alloy. Abrasive wear tests were carried out when samples glided on polished paper (fused corundum with a grain size of 18 μm). We analyzed a wear track at a linear gliding velocity of 0.3 m/s and a normal load of 50 N for the CMs based on cobalt, iron, nickel, and titanium and a load of 10 N for the CMs based on copper, nickel, and aluminum-based alloy. The abrasive wear was determined from the CM mass loss for a wear path of 9 m.

RESULTS AND DISCUSSION

The XRD investigation of the samples showed that the interaction of carbon with a metallic matrix under nonequilibrium synthesis conditions (high pressure, short holding time) leads to the appearance of carbides TiC, Fe_3C, and Ni_3C in them. The cobalt-based CM synthesized at a pressure of 8 GPa contains carbides Co_3C and Co_2C, and the possibility of their formation in the Co–C system under such a pressure was shown in [14]. Table 1 gives the properties of the reinforcing carbon phase after synthesizing CMs under various conditions.

The interaction of nickel with carbon during synthesis results in the appearance of graphite in CM, and it was detected by Raman spectroscopy of the nickel-based CM (Fig. 1). Asymmetric Raman spectrum *1* recorded from the center of the carbon particle is typical of a high-hardness carbon phase [15]. Raman spectra *2* and *3*, which were recorded from the regions at the carbon-particle/Ni-matrix interface and from the black inclusion at the junction of nickel grains, exhibit broadened peaks, which are similar to the D and G peaks of carbon and correspond to random graphite [15].

The iron-based CM matrix has the entire spectrum of solid solutions of carbon in iron (martensite, austenite, ferrite) and Fe_3C carbides (Table 2). No compounds of matrix metals with carbon were detected in the CM matrices based on the aluminum alloy and copper and synthesized at a pressure of 5–8 GPa.

The reinforcing carbon phase in the metallic matrices under study is characterized by a high indentation hardness (H_{IT} = 10–37 GPa) and elastic modulus (61–261 GPa; see Table 1). Preliminary mechanical activation of the initial fullerites increases the hardness of reinforcing carbon particles to H_{IT} = 31–37 GPa and decreases the elastic recovery upon indentation to 79–84% (see Table 1, Fig. 2). In this case, the tribological properties of the reinforced CMs are substantially improved. Simultaneously, the abrasive wear resistance increases and the friction coefficient decreases (see Table 1). The ratio of the indentation microhardness to the elastic modulus (H_{IT}/E_{IT}) of

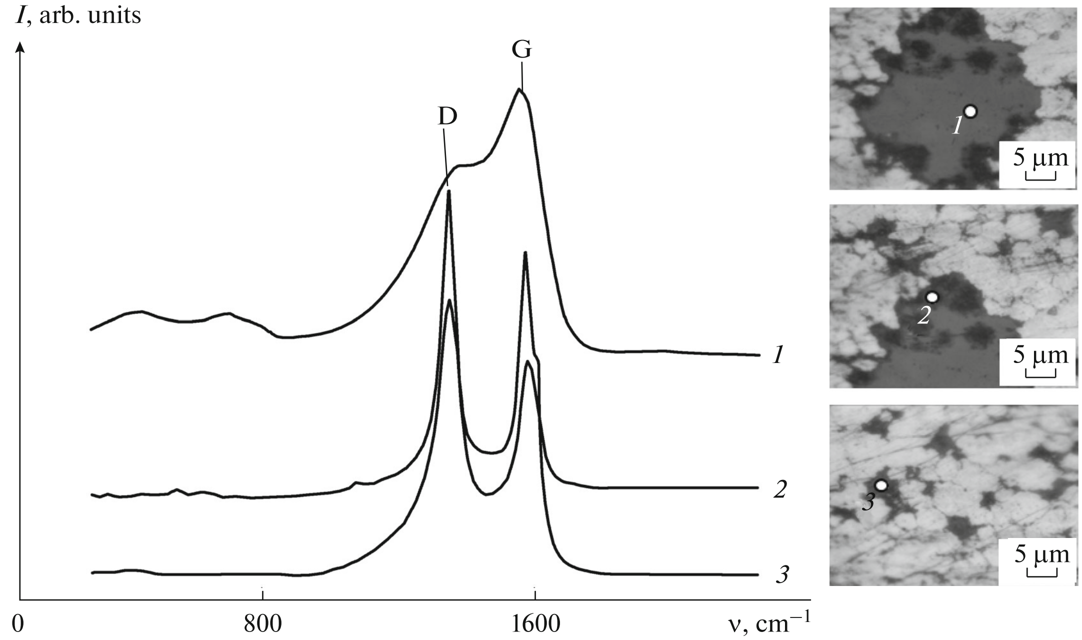

Fig. 1. (on the left) Raman spectra *1–3* and (on the right) microstructure of carbon phases in nickel-based CM. (*1–3*) Points of recording the Raman spectra at the center of the carbon particle, at the particle/matrix interface, and in the black inclusion at the junction of nickel grains, respectively.

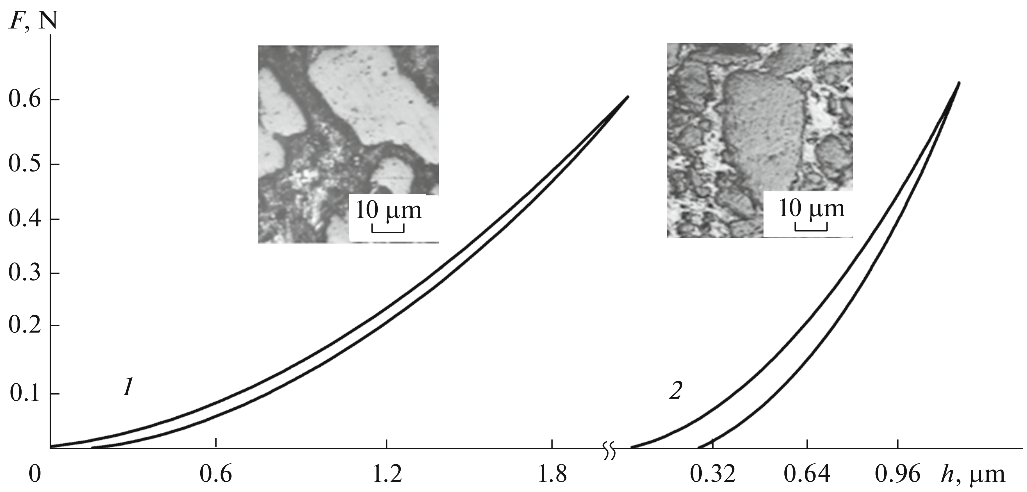

Fig. 2. Indentation curves (*h* is the indenter penetration depth) of the carbon particles formed from a mixture of $C_{60/70}$ fullerites under the following CM synthesis conditions: (*1*) at a pressure of 5 GPa and a temperature of 700°C (H_{IT} = 10 GPa, R = 93%), AK12M2MgN-based CM; (*2*) at 8 GPa and 800°C (H_{IT} = 31 GPa, R = 83%), copper-based CM.

reinforcing particles decreases slightly. A correlation between the improvement of the tribological properties of CMs and the parameter H_{IT}^2/E_{IT} of the particles was detected. The role of hardness in this parameter is seen to be enhanced [16].

To estimate the influence of reinforcing particles on the friction coefficient, the results of tribological tests of CMs were compared with the data obtained for samples formed by the same thermobaric treatment from metal powders without fullerites (see Table 2). An analysis of the tribological properties and the wear resistance of the CMs reinforced by superelastic hard carbon particles showed that the tribological properties of all metals are substantially improved upon reinforcing. The friction coefficient of CM decreases as compared to that of the matrix material by a factor of 2–4: from 0.57 to 0.24 for Fe, from 0.56 to 0.23 for the AK12M2MgN alloy, from 0.49 to 0.2 for Ni, from 0.48 to 0.17 for Co, and from 0.8 to 0.4 for Cu. The effect of decreasing the friction coefficient upon reinforcing a

Table 2. Phase compositions and properties of a matrix material without reinforcing by carbon particles and CM: friction coefficient ($f_{fr\,M}$, $f_{fr\,CM}$) and mass loss during abrasive wear (Δm_M, Δm_{CM})

CM matrix	Phase composition of CM matrix	$f_{fr\,M}$	$f_{fr\,CM}$	$\frac{f_{frM}}{f_{frCM}}$	Δm_M	Δm_{CM}	$\frac{\Delta m_M}{\Delta m_{CM}}$
					mg		
AK12M2MgN	Al + Si	0.56	0.23	2.4	19.60	4.80	4.1
Ti	Ti + TiC	0.79	0.26	3.0	22.40	3.20	7.0
Fe	Martensite, austenite, ferrite, Fe_3C	0.57	0.24	2.3	—	1.60	—
Cu	Cu	0.80	0.20	4.0	30.90	0.35	88
Ni	Ni + Ni_3C + graphite	0.49	0.20	2.5	44.00	7.30	6.0

metal by superhard superelastic carbon particles is schematically illustrated in Fig. 3.

The friction coefficient of CM correlates with that of the corresponding metal without reinforcing: the lower the friction coefficient of the metal, the lower the friction coefficient of CM in the row Cu, Ti, Fe, Al, Ni, and Co (see Table 2).

The character of changing the friction coefficient also changes when a metal is reinforced by a superelastic carbon phase: the time instability of the friction coefficient decreases (Figs. 4, 5).

The reinforcing of all metals by superelastic carbon increases the abrasive wear resistance by a factor of 4–200 (see Table 2). The wear resistance of CM mainly

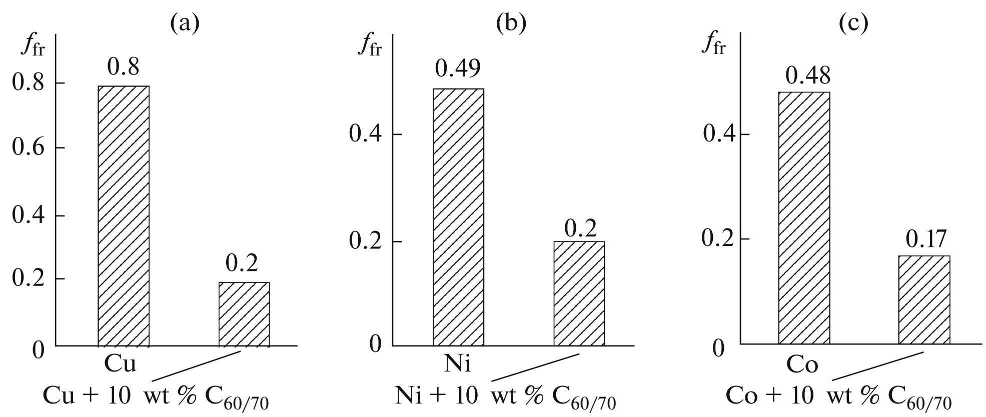

Fig. 3. Friction coefficients of metals ((a) Cu, (b) Ni, (c) Co) and the related CMs with 10 wt % particles formed from a mixture of $C_{60/70}$ fullerites under pressure. The indentation microhardness of the CMs is H_{IT} = (a) 31, (b) 35, and (c) 37 GPa, respectively.

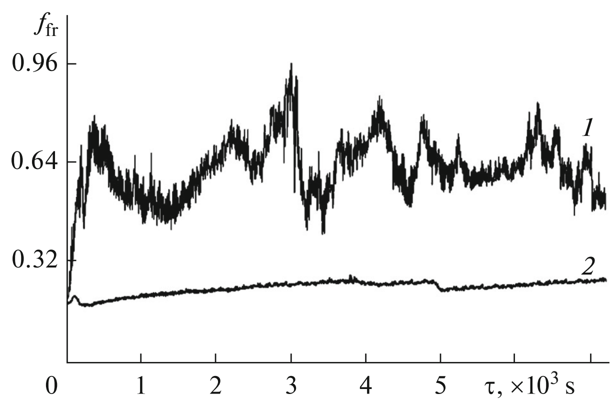

Fig. 4. Kinetic dependences of the friction coefficient of (*1*) AK12M2MgN alloy and (*2*) AK12M2MgN-based CM reinforced by superelastic hard carbon particles.

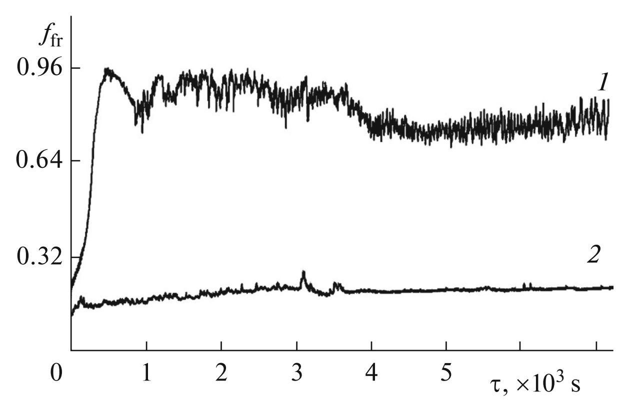

Fig. 5. Kinetic dependences of the friction coefficient of (*1*) titanium and (*2*) titanium-based CM reinforced by superelastic hard carbon particles.

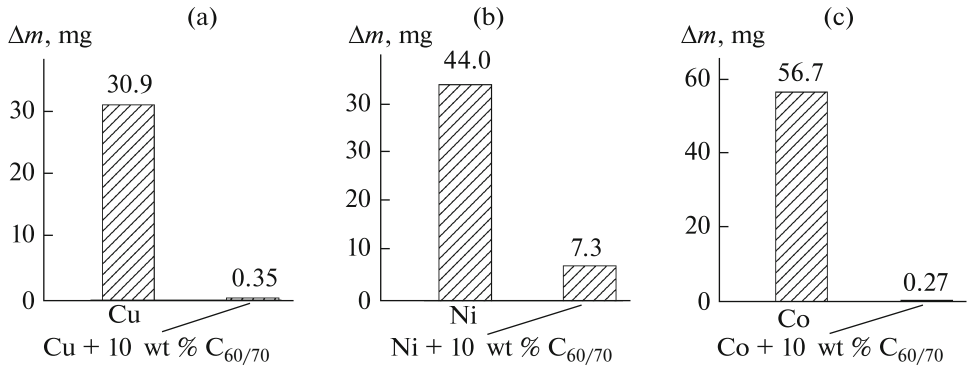

Fig. 6. Abrasive wear (mass loss) of metals (a) Cu, (b) Ni, and (c) Co and the related CMs with 10 wt % particles formed from a mixture of $C_{60/70}$ fullerites under pressure. The indentation microhardnesses of the CMs are given in the caption to Fig. 3.

depends on the hardness of the superelastic hard carbon phase. For example, the presence of titanium carbides in the titanium-based CM at a relatively low microhardness of reinforcing carbon particles (H_{IT} = 14 GPa) results in a sevenfold increase in the wear resistance, and the wear resistance of the copper-based CM reinforced by carbon particles with a microhardness H_{IT} = 31 GPa increases by 88 times. The wear resistance of CM depends substantially on the phase composition of the matrix. Due to the presence of graphite in the nickel-based CM, its wear resistance increased sixfold as compared to pure nickel, and the wear resistance of the cobalt-based CM at the same hardness of the reinforcing particles is higher than that of pure cobalt by a factor of 210 (Fig. 6).

CONCLUSIONS

(1) We synthesized metal-matrix CMs made of a metallic powder (Ti, Fe, Co, Ni, Cu, Al-based alloy) and 10 wt % $C_{60/70}$ fullerene mixture at a temperature of 700–1000°C and a pressure of 5–8 GPa. Phase analysis of the CMs showed that the interaction of carbon with a metallic matrix under nonequilibrium synthesis conditions (high pressure, short holding time) leads to the formation of carbides (TiC, Fe_3C, Co_3C, Co_2C, Ni_3C) in the structure of CM and the formation of graphite in a nickel matrix. The iron-based CM matrix contains martensite, austenite, ferrite, and Fe_3C carbides. No compounds of matrix metals with carbon were detected in the CM based on the AK12M2MgN aluminum alloy or copper.

(2) The structure and properties of the carbon phase that forms from fullerites do not depend on the chemical composition of the matrix and are determined by the CM synthesis conditions. The following changes were detected after synthesis and preliminary mechanical activation of fullerites: the indentation microhardness of reinforcing particles H_{IT} increased from 10 to 37 GPa, the elastic modulus increased from 60 to 260 GPa, and the elastic recovery decreased from 96 to 79%.

(3) The reinforcing of a metallic matrix based on a certain metal (Cu, Ti, Fe, Al, Ni, Co) by a hard carbon phase improves the tribological properties of the synthesized CMs. The friction coefficient of the CMs decreases by a factor of 2–4 as compared to the matrix metal (from 0.57 to 0.24 for Fe, from 0.56 to 0.23 for the AK12M2MgN alloy, from 0.49 to 0.2 for Ni, from 0.48 to 0.17 for Co, and from 0.8 to 0.2 for Cu). The friction coefficient of CM depends on the friction coefficient of the matrix metal: the lower the friction coefficient of the matrix metal, the lower the friction coefficient of CM in the row Cu, Ti, Fe, Al, Ni, and Co.

(4) The reinforcing of the metals under study by superelastic hard carbon increases their abrasive wear resistance by a factor of 4–210. The wear resistance of CM depends on the hardness of the superelastic hard carbon phase and the phase composition of the matrix. Due to the presence of graphite in the nickel-based CM, its wear resistance increases sixfold as compared to pure nickel, and the wear resistance of the cobalt-based CM at the same hardness of the reinforcing particles is higher than that of pure cobalt by a factor of 210.

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