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MAGNETIC PARTICLES
AND NANOCRYSTALLINE MATERIALS

The Research of Powder Fullerene and Ultra-Dispersed Diamond Composites with Metal and Oxide Nanoparticles[1]

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Abstract—Magnetic properties of new nanophase materials based on oxide and metal particles of *d* transition metals included in the powder fullerite C_{60} and detonative ultradispersed diamonds (UDD) are investigated. The materials are obtained by an original method of catalytic combustion reaction.

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1. INTRODUCTION

In the elaboration of new nanophase materials, one of the most pressing problems is obtaining magnetic nanoparticles spread in a magnetically neutral matrix by the direct interaction of the reagents in one-stage synthesis. In our earlier works, it was shown that the thermic interaction in solid-state powder mixtures of fullerene C_{60} and iron (III) acetylacetonate proceeds in a catalytic combustion regime. The products of thermal reactions can be obtained in the form of powder composites consisting of dispersed particles of Fe_3O_4 and fullerite [1].

The purpose of this work is the research and synthesis of powder composites on the basis of fullerite C_{60} and ultradispersed diamonds with metal and oxide nanoparticles of *d* transition metals included. The peculiarity of this material is that magnetic particles are located in a magnetically neutral but chemically active matrix.

2. EXPERIMENTAL

For synthesis of target materials, powder mixtures $M(acac)_n/C_{60}$ and $M(acac)n$/UDD (1:1) (where $acac^- = CH_3COCHCOCH_3^-$; M = Fe, Ni, Co, Cr, Cu; Pt, Ir, Pd; and n is the oxidation degree of M) were heated to the visible burning of the mixture. Air access to the mixture was limited for the reaction to proceed without flame formation. Under such conditions, the gasification of C_{60} and UDD practically does not occur. External heating (~300°C) was kept during the combustion process (series S_1). After ignition (flare up) of the mixture, the heating was stopped and the reaction went on in the self-maintaining regime (series S_2). During research of the $Fe(acac)_3/C_{60}$ system, the stoichiometric ratio of the reagents was varied as Fe : C_{60} = 1 : 1, 2 : 1, 5 : 1, 1 : 2 for the samples $S_1$2/1, $S_1$5/1, $S_2$1/2, $S_2$1/1, and $S_2$2/1, respectively.

The electron magnetic resonance (EMR) spectra were recorded with an SE/X-2544 EPR spectrometer. The iron state was determined with the help of Mössbauer measurements executed with a source of ^{57}Co (Cr). The magnetic measurements were carried out with a vibrating-sample magnetometer. The X-ray diffusion phase analysis data were obtained on a laboratory powder diffractometer using Cu $K\alpha$ radiation.

3. RESULTS AND DISCUSSION

The pyrolysis of volatile acetylacetonates of 3*d* transition metals in air occurs with their transformation into

Table 1. Parameters of the EMR spectra of the combustion products of $M(acac)_n/C_{60}$ and $M(acac)_n$/UDD mixtures

M		Line of metal		Line of radical	
C_{60}	UDD	g	ΔH, mT	asymmetric	ΔH, mT
Fe		2.23	120		–
Ni		2.12	50	0.86	0.26
Co		~2.1	200	0.87	0.9
Cr		1.98	90	0.88	0.3
Cu		2.11	20	0.88	0.55
Ir		2.4	100	Dyson shape	
Pt				0.55	0.06
Pd		2.35	140	0.78	0.12
	Fe	2.01	85		–
	Cu	2.06	62		0.1

[1] The text was submitted by the authors in English.

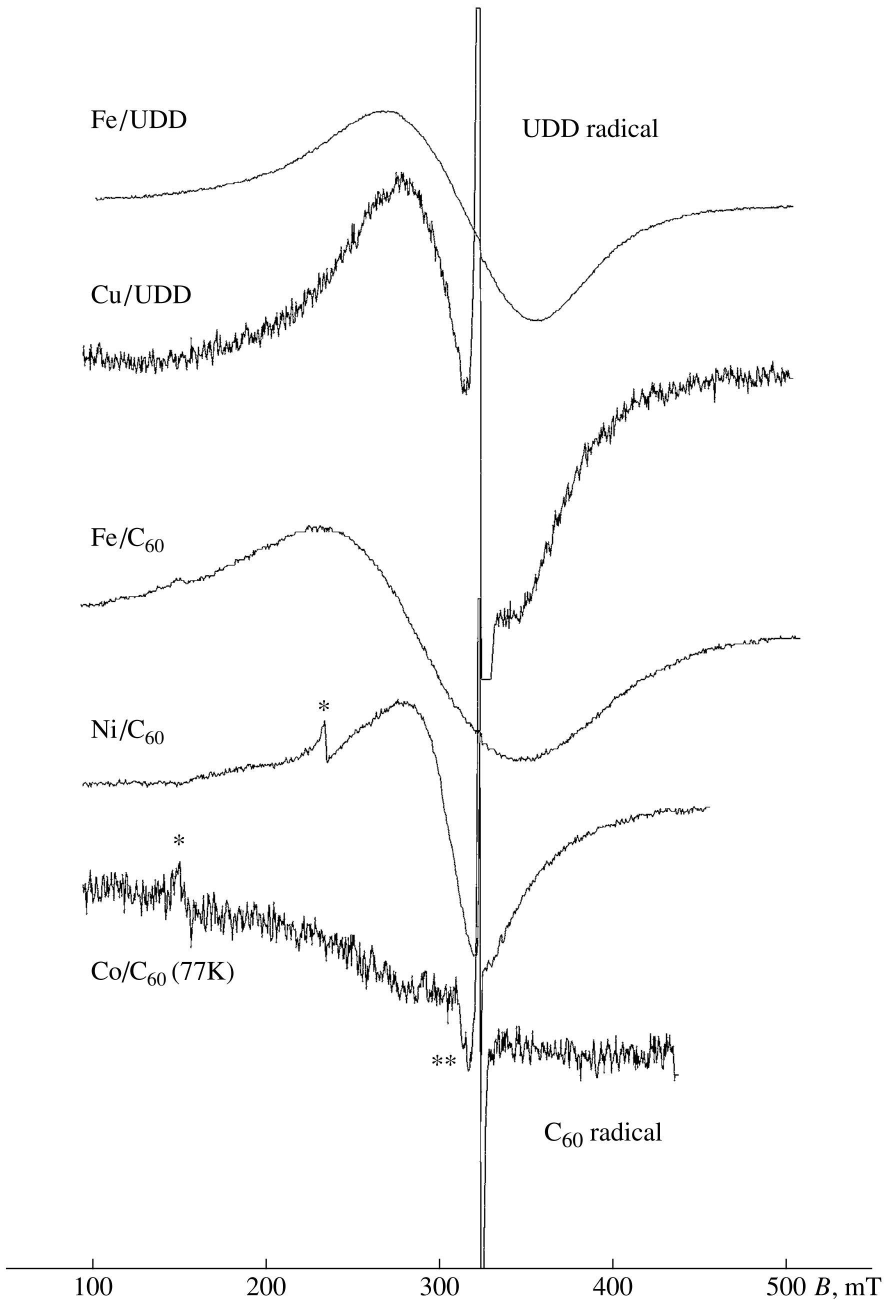

Fig. 1. EMR spectra of the combustion products of 3*d* transition-metal acetylacetonates in mixtures with C_{60} and UDD: (**) metal particles of Co; and (*) metal in a pipe.

metal oxides; acetylacetonates of platinum metals educe free metal [2]. X-ray diffraction analysis of powder materials formed as a result of combustion of C_{60} (or UDD)/$M(acac)_n$ mixtures showed that they contain metal and oxide particles in a highly dispersed state alongside with a nanocarbon phase. The observed reflections from metal-containing phases are highly broadened or absent. The parameters of the EMR spectra of the combustion products (series S_1) are shown in Table 1; the spectra are given in Figs. 1, 2. The powder materials synthesized on the basis of Cu, Co, and Cr complexes and C_{60} are characterized by a low absorption of microwave power, which slightly increases with cooling to 77 K. The resonance lines are broadened. It is known [3] that the oxides of these metals are antiferromagnetic; the observed absorption is determined by magnetic atoms being on the oxide-particle surface. The weak absorption indicates that the linear sizes of particles are ~100 nm. The EPR line of the C_{60} radical, which is characteristic of fullerite, is also observed and has a slightly asymmetric form. The combustion products of $Ni(acac)_2/C_{60}$ absorb microwave power much

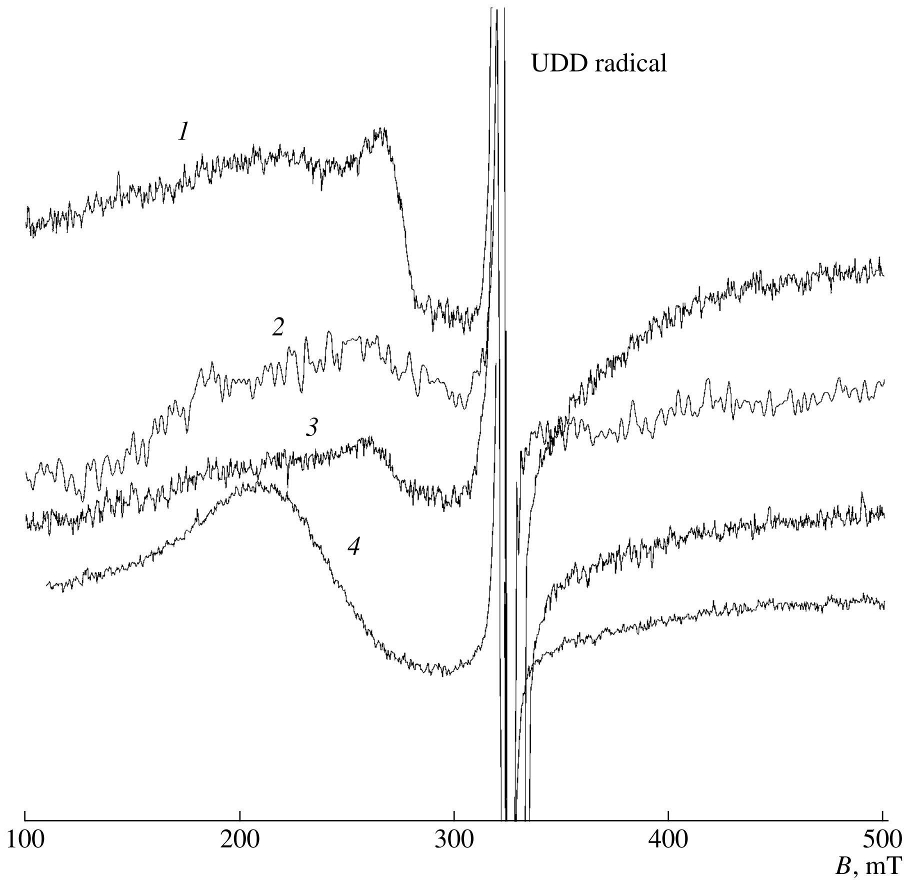

Fig. 2. EMR spectra of the combustion products of $M(acac)_n$/UDD mixtures: (*1*) Pd$(acac)_2$/UDD; (*2*) Pt$(acac)_2$/UDD; (*3*) Ir$(acac)_3$/UDD (at 293 K); and (*4*) Ir$(acac)_3$/UDD (at 77 K).

more actively as compared to the listed samples. The EMR-spectrum parameters for them coincide with those obtained in [4] for metal Ni particles of a diameter 50–100 nm in a paraffin matrix. In the spectra of Cu- and Co-containing materials, there are weak lines of asymmetric form (see Fig. 1). We assume that they are caused by the presence of small quantities of metal particles (of size ~10 nm) alongside with oxide particles. The EMR spectra of the $M(acac)_n$/UDD combustion products show that all of them are reduced to metal. This follows from the asymmetric form of the resonance line [5]. The materials synthesized are powder mixtures of UDD and metal particles, with linear sizes of ~100 nm.

According to Mössbauer spectroscopy and X-ray diffraction data, the burning of Fe$(acac)_3$/C_{60} results in the conversion of Fe$(acac)_3$ mainly to magnetite. The EMR spectra and magnetic measurement of the products of thermal synthesis (Table 2) show the dependence of the material magnetic properties on the composition of the initial mixture and the temperature conditions of synthesis. An increase in the amount of Fe$(acac)_3$ relative to C_{60} increases the magnetization, the resonance-line width, and the *g* factor. A quantitative conversion of Fe$(acac)_3$ to magnetite and an increase in the dispersion of metal-containing particles were observed under S_2 conditions. For the samples of the S_2 series, the size of metal-containing particles is from 20 to 6 nm, decreasing with decreasing metal concentration in the initial mixture. The magnetite-particle sizes in the samples are determined from the measured

Table 2. Parameters of the EMR spectra of the combustion products of Fe$(acac)_3$/C_{60}

Samples	$S_1$2/1	$S_1$5/1	$S_2$2/1	$S_2$1/1	$S_2$1/2
σ, emu/g					
300 K			235	237	2.25
77 K			201	225	2.0
g_{eff}					
300 K	2.2	2.4	2.26	2.24	2.15
77 K			2.65	2.36	2.2
ΔH, kA/m					
300 K	132	150	98	57	87
77 K			105	85	120
Diameter of particles, nm	150	film	20	15	13–6

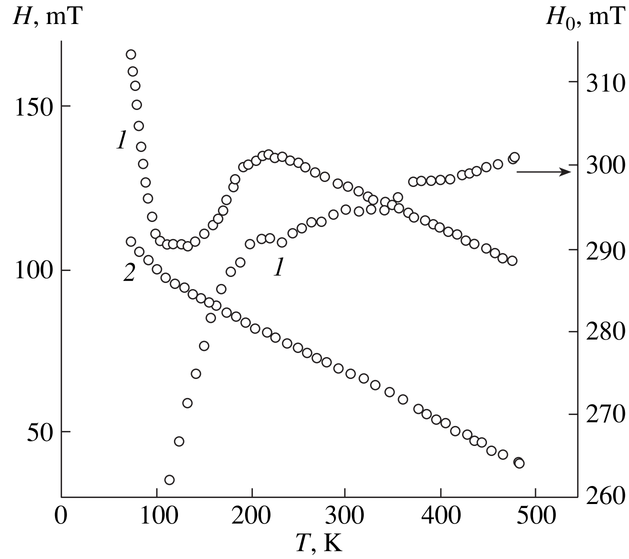

Fig. 3. Temperature dependences of the EMR parameters (ΔH and H_0) of the powder Fe_3O_4/C_{60} composites: (*1*) $S_22/1$ and (*2*) $S_21/1$.

EMR linewidths with the data used in [5]. The temperature behavior of resonance in the $S_21/2$ system is determined by the superparamagnetic state of magnetite nanoparticles [6]. In Mössbauer spectra, a paramagnetic phase is registered, indicating a connection between the surface atoms of Fe and fullerene which is due to a decrease in the particle size.

Figure 3 shows the temperature dependences of the EMR characteristics for magnetic particles in samples $S_21/1$ and $S_22/1$. From 200 to 110 K, a narrowing of the EMR lines (Fig. 3) is observed for $S_22/1$; then, at 100 K the line width dramatically goes up. The magnetization temperature behavior depends on the magnetic field direction [6]. The complex of effects observed in the sample allows one to conclude that there occurs a transition to a spin-glass state; the connection between particles is carried out through fullerene molecules. As the magnetite-particle size is reduced and the fullerite dilution increases, the connection between them becomes weaker. For this reason in the temperature range of down to 77 K we did not observe such a transition for the sample $S_21/1$.

One peculiarity of the EMR of powder materials obtained in thermal processes with the participation of fullerite C_{60} and Pt-metal acetylacetates is the resonance line of an asymmetric form characteristic of metal particles [7]. The EPR lines of the C_{60} radical also have a significant asymmetry (see Table 1). For an Ir-containing sample, a Dyson shape of the resonance line characteristic of electrons in the conduction band of the metal was observed. Probably, there is formed a metal coating on fullerite grains. In similar processes with UDD, powder composites with particles of the metal are formed.

4. CONCLUSIONS

New powder nanomaterials have been synthesized. They represent composites consisting of highly dispersed metal and oxide particles of 3*d* transition metals with powder fullerite C_{60} and UDD. It is shown that it is possible to change the sizes of particles and their magnetic properties directly by varying the parameters of the synthesis process which is based on a catalytic combustion of volatile acetylacetonate of *d* transition metals initiated by fullerite C_{60} and UDD. With platinum metals, powder mixtures of UDD with highly dispersed metal-particle inclusions and films of metals on the surface of a fullerene grain are obtained.

REFERENCES

1. V. G. Isakova, E. A. Petrakovskaya, A. D. Balaev, et al., Zh. Prikl. Khim. **76**, 597 (2003).
2. *Problems of Chemistry and Application of Metal β-diketonates*, Ed. by V. Yu. Spitsin (Nauka, Moscow, 1982) [in Russian], p. 246.
3. S. V. Vonsovsky, *Magnetism of Microparticles* (Nauka, Moscow, 1973) [in Russian], p. 280.
4. Yu. I. Petrov, *Physics of Small Particles* (Nauka, Moscow, 1982) [in Russian], p. 359.
5. S. M. Aharoni and H. M. Litt, J. Appl. Phys. **42**, 3 (1971).
6. E. A. Petrakovskaya, V. G. Isakova, A. D. Balaev, et al., Izv. Ross. Akad. Nauk, Neorg. Mater. **40**, 682 (2004) [Inorg. Mater. **40**, 589 (2004)].
7. T. A. Fedushchak and A. P. Il'yin, Zh. Prikl. Khim. **75**, 359 (2000).