Preparation of ultrafine metal particles in processes of pulse mechanical action

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Ultrafine metal particles (UFMP) (iron and cobalt) have been obtained in solid-state redox reactions of cyclopentadienyl-π-(3)-1,2-dicarbollyliron or cyclopentadienyl-π-(3)-1,2-dicarbollylcobalt with elemental sulfur ($(C_5H_5)Fe^{3+}(C_2B_9H_{11})$—S, $(C_5H_5)Co^{5+}(C_2B_9H_{11})$—S). These reactions are realized by the action of elastic wave (EW) pulses on powder compositions of these substances. Study of the UFMP obtained by the ferromagnetic resonance (FMR) method has shown that the sizes of $n \cdot Co^0$ UFP lie in the range from 1 to 13 nm. UFP of cobalt and iron are also formed under the action of EW on samples containing $(C_5H_5)Fe^{3+}(C_2B_9H_{11})$—S or $(C_5H_5)Co^{3+}(C_2B_9H_{11})$—S within the film of tetrafluoroethylene and perfluoro-4-methyl-3,6-dioxaoct-7-ene-1-sulfonyl fluoride copolymer (CP). It is shown by the FMR method that FMR lines broaden on going from powder systems to systems containing CP films. It is supposed that $n \cdot Co^0$ and $n \cdot Fe^0$ particles interact with polymeric matrices in the course of formation and stabilization of UFMP in the matrices.

Key words: cyclopentadienyl-π-(3)-1,2-dicarbollylcobalt, cyclopentadienyl-π-(3)-1,2-dicarbollyliron, sulfur, ferromagnetic resonance, ultrafine metal particles, solid-state synthesis, pulse, elastic wave.

The methods of low-temperature co-condensation of metal vapor and organic substances,[1] reduction of metal salts in a swollen "polyacrylic acid—urea-formaldehyde polymer" complex,[2] and matrix reactions in the thermolysis of cationic complexes of arenecyclopentadienyliron type based on arylenecarborane oligomers[3] are currently widely used for preparing ferromagnetic ultrafine metal particles (UFMP). In all cases, the properties of ferromagnetic UFMP are determined by their composition, structure, and size. All of the aforementioned chemical methods for preparing such UFMP in matrices are associated with many preparative procedures. Therefore, the development of new methods for preparing ferromagnetic UFMP and simultaneously introducing them into polymeric matrices is an urgent problem.

It has previously[4] been established by the ESR method that oriented ultrafine copper sulfate clusters can be formed in the polymeric matrix in the process of "pressure explosion" of "sandwich" polymer—$CuSO_4 \cdot 5H_2O$ samples. Polyethylene and polypropylene of various trade marks were used as polymers. However, no deep reduction to metal particles of the $n \cdot Cu^0$ type was observed. Therefore, the purpose of this work was to elucidate the possibility of preparing ferromagnetic UFMP upon pulse mechanical action with simultaneous introduction of UFMP into a polymeric matrix. The application of the ferromagnetic resonance (FMR) method, ESR for ferromagnetic particles,[1–3] that can detect 10^{15} particles in 1 cm^3 can be extremely useful.

Experimental

Compounds with various redox properties, cyclopentadienyl-π-(3)-1,2-dicarbollyliron(III) ($(C_5H_5)Fe^{3+}(C_2B_9H_{11})$ (**1**)) and cyclopentadienyl-π-(3)-dicarbollylcobalt(III) ($(C_5H_5)Co^{3+}(C_2B_9H_{11})$[5] (**2**)), were used. Elemental sulfur (S) as the reducing agent and sulfur-containing copolymer (CP) of tetrafluoroethylene and perfluoro-4-methyl-3,6-dioxaoct-7-ene-1-sulfonyl fluoride (CF_2=CF—O—CF_2—CF(CF_3)—O—CF_2—CF_2—SO_2F)[6] were used. The copolymer has a comb-like structure, and the content of the second comonomer is ~12 mol. %. This CP was chosen as an object of studies, because side branches with the corresponding terminal functional groups form nanorange clusters in which diffusion processes are considerably facilitated compared to the perfluorinated matrix.[6]

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2355—2358, December, 1995.

1066-5285/95/4412-2251 $12.50

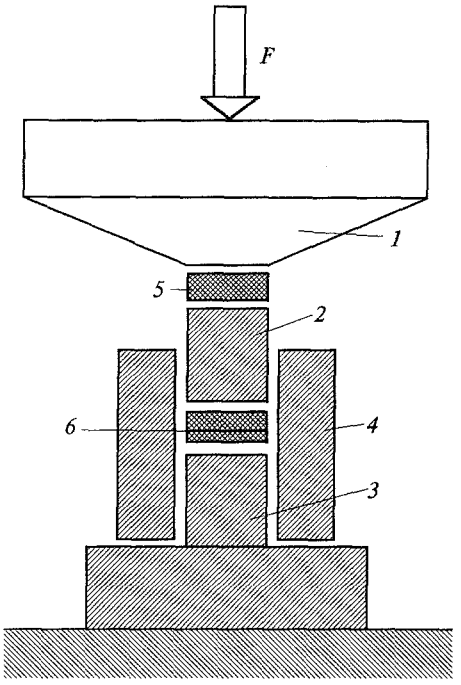

Fig. 1. Scheme of the setup for pulse mechanical action: *1*, Bridgeman anvil, *2*, wave guide, *3*, punch, *4*, holder, *5*, PP plate, *6*, sample.

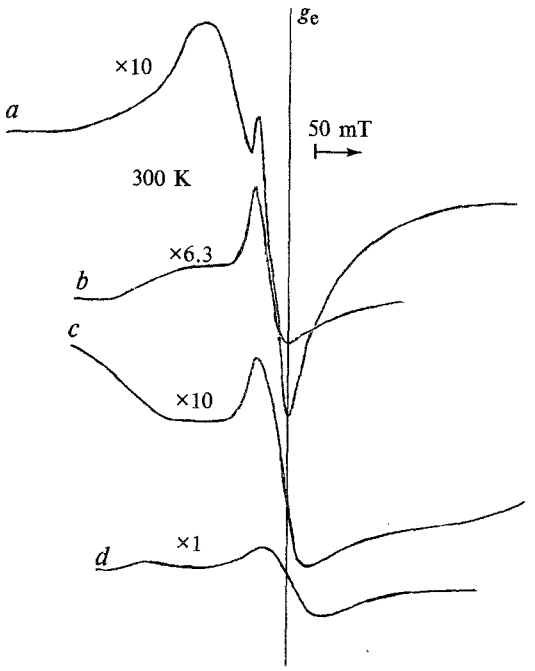

Fig. 2. FMR spectra of products of the pulse mechanical treatment of powder mixtures with various weight ratios of the initial components in the powders: **2** : S = 1 : 1 (*a*); **2** : S = 2 : 1 (*b*); **1** : S = 1 : 1 (*c*); **1** : S = 2 : 1 (*d*).

The pulse mechanochemical action was carried out in a setup shown in Fig. 1. This setup makes it possible to realize the explosion-induced elastic wave (EW) action on samples under study (*6*) mediated by the pressure of polypropylene (PP) plates (*5*).[7] The samples were placed inside a steel holder (*4*) between a wave guide (*2*) and a punch (*3*), they comprised either molded pellets **1**, **2**, **1**—S, and **2**—S or thin CP films (150 μm) between which molded pellets **1**, **2**, **1**—S, and **2**—S were placed (in all experiments the widths of these pellets did not exceed 200 to 250 μm). Only the portion of the samples used that remained between *2* and *3* after the EW action, was examined. A portion of the sample, which was squeezed into the gaps between holder *4* and *2*—*3* was not studied at all, because it was subjected to an additional action of shearing deformations during extrusion to the gaps. All experiments were carried out in air.

FMR spectra were recorded on Varian E-12 and Radiopan spectrometers with a working frequency of 9.1 GHz.

Results and Discussion

It is established by the FMR method that the treatment of powders of individual compounds **1** or **2** under the conditions of EW action does not result in the formation of ferromagnetic UFMP in these compounds. The EW treatment of a mixture of **1** or **2** with elemental sulfur results in chemical transformations yielding ferromagnetic UFMP registered by the FMR method (Fig. 2).

The FMR spectrum of a 1 : 1 **2**—S mixture (the ratios herein are given in mass fractions) contains two lines with g_{eff} = 2.17 and the widths ΔH = 35 and 100 mT (see Fig. 2, *a*), while that of a 2 : 1 **2**—S mixture contains one asymmetric line with g_{eff} = 2.17 and the width ΔH = 40 mT (see Fig. 2, *b*). In the case of the iron derivative, the FMR spectrum with g_{eff} = 2.05 and ΔH = 60 mT was recorded for a 1 : 1 **1**—S mixture (see Fig. 2, *c*), and that with g_{eff} = 2.0 and ΔH = 67 mT for a 2 : 1 **1**—S mixture (see Fig. 2, *d*).

The formation of similar FMR spectra has been also observed for CP—(**1**—S) and CP—(**2**—S) samples. It is seen that the structures of the spectra in Fig. 3 differ from those presented in Fig. 2: all of them occupy a broader magnetic field range due to the superposition of several FMR lines with various widths. The lines with widths of 35, 100, 250, and 350 mT are registered for samples (**2**—S)—CP, (1 : 1) : CP (see Fig 3, *a*), while samples (**2**—S)—CP, (2 : 1) : CP exhibit the lines with widths of 35, 100, and 250 mT (see Fig. 3, *b*). Samples (**1**—S)—CP, (1 : 1) : CP exhibit the lines with widths of 25, 65, and 175 mT, and samples (**1**—S)—CP, (2 : 1) : CP have the lines with widths of 60 and 175 mT. It is also seen from the spectra presented in Figs. 2 and 3 that the intensities of FMR lines and their ratios differ for both samples with different compositions of the starting components and for the samples containing CP films. Thus, magnetic products are formed likely due to the decomposition of metallocarboranes **1** and **2** under the conditions of EW action upon systems **1**—S, **2**—S, (**1**—S)—CP, and (**2**—S)—CP.

The determination of structures of magnetic products from FMR spectra is the most reliable in the case of reaction of **2** with sulfur, because no FMR of the Co^{2+}

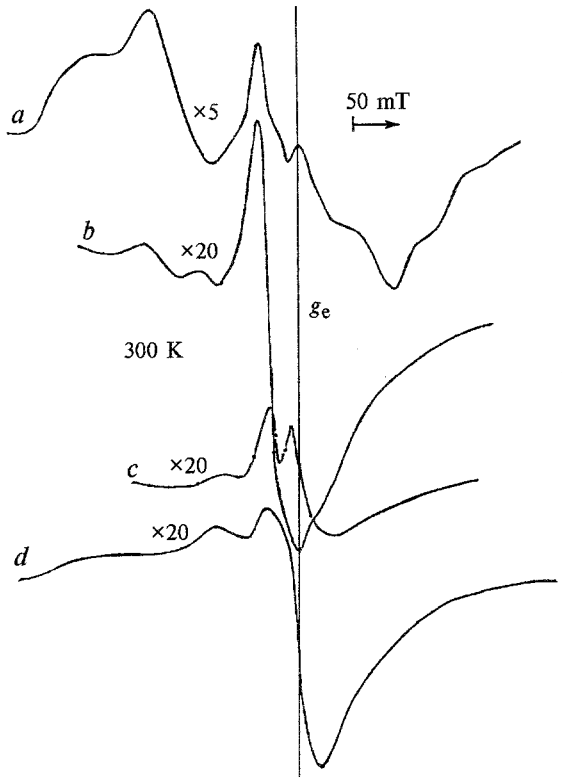

Fig. 3. FMR spectra of products of the pulse mechanical treatment of CP—powder mixture—CP samples with various weight ratios of the initial components in the powders: **2** : S = 1 : 1 (*a*); **2** : S = 2 : 1 (*b*); **1** : S = 1 : 1 (*c*); **1** : S = 2 : 1 (*d*).

ion is observed at usual temperatures, and cobalt UFP have a characteristic spectrum with the effective *g*-factor equal to 2.2. In addition, a qualitative correlation exists between the FMR line width and UFP size of cobalt particles.[8,9] It is known that the FMR line width, depending on the size of cobalt UFP, takes the values of 20 mT for d = 1 nm,[9] 50 mT for d = 5 nm, and 170 mT for d = 13 nm.[8] The oxidation of the UFP surface results in a dramatic increase in the line width: ΔH was ~300 mT for oxidized particles with the mean size of ~3 nm.[1] The analysis of the spectra of systems **2**—S presented in Figs. 2 and 3 shows that the absorption maximum of all ESR lines corresponds to the effective value g_{eff} = 2.17. A decrease in the weight content of **2** relative to S in the samples (see Fig. 2, *a*,*b*) affects noticeably the intensity of absorption and the width of the asymmetric line, which is ~35—40 mT.

The FMR spectra of particles injected into CP films are characterized by a great scatter in the line width (see Fig. 3, *a*,*b*) and occupy the field range from zero to 500 mT, *i.e.*, a complicated pattern of superposition of several lines takes place.

There are two reasons for the increase in the line widths for UFP in CP: (1) a thicker oxide film of UFP in CP, which results in a substantial increase in the line width, and (2) an increase in the mean size of UFMP in the CP film compared to those of UFP in powders of individual compounds due to some aggregation of particles upon penetration into the CP film under the EW action. Presently, it seems impossible to analyze all the aspects of the effect of compositions of reaction mixtures and the nature of polymeric films on FMR spectra of cobalt UFP. However, comparing the results obtained with the literature data,[1,8,9] one may assert that the size distribution of cobalt UFP obtained falls in the range of 1 to 13 nm.

In all FMR spectra of compound **1** the absorption maxima correspond to g_{eff} = 2.00, and an increase in line widths or appearance of new lines is also observed on going from powders to CP films (see Figs. 2 and 3). However, unambiguous identification of iron UFP from the FMR spectra is possible only in rare cases of narrow line widths that are observed for fine particles. Therefore, only lines with ΔH equal to 25—30 mT can be assigned to iron UFP.[3] In other cases, it seems impossible to separate contributions of ferromagnetic iron and paramagnetic oxides.

Basically physical reasons do not allow one to determine the concentration of ferromagnetic particles. In fact, in monodomain and polydomain UFP each domain is magnetized to saturation in the absence of an external magnetic field. Therefore, the domain absorbs the high-frequency energy in FMR experiments in a different way than free radicals used in reference samples for determining the amount of paramagnetic particles. However, it can be asserted that the UFMP concentration is sufficiently low, because the existence of UFMP could not be distinctly detected by small-angle X-ray scattering for either of the samples.

Basing on the results obtained, one can draw a conclusion that the EW pulse action upon a mixture of carboranes **1** and **2** with elemental sulfur results in the decomposition of **1** and **2** yielding a metal followed by its aggregation to UFMP. It is evident that in these processes the formally trivalent iron and cobalt atoms undergo several subsequent redox acts. It is established that the polymeric matrix also participates in the formation of UFMP. Thus, the possibility to synthesize ferromagnetic UFMP by the pulse mechanical action and simultaneously introduce them into a polymeric matrix has been shown for the first time.

The study of particular stages of these process is the subject of further works.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 94-03-09632).

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Received May 25, 1995;
in revised form July 12, 1995