Journal of Engineering Physics and Thermophysics, Vol. 73, No. 3, 2000

MODIFICATION OF THE ADSORPTION PROPERTIES OF THE DISPERSED PHASE OF MAGNETORHEOLOGICAL LIQUIDS

S. R. Gorodkin,[a] **V. N. Makatun,**[b]
S. V. Matveichuk,[b] **and Z. A. Novikova**[a]

UDC 532.135:699.127.42

A rather simple method for modifying the surface of powder carbonyl ion – the most widespread material of the active dispersed phase of magnetorheological liquids – is developed. It is shown that the specimens of liquids prepared based on modified carbonyl iron have an improved sedimentation stability, a viscosity severalfold lower than the initial one, and hence an expanded control range of rheological parameters when the magnetorheological effect is the same as in reference specimens.

Introduction. Finely divided iron with a particle size of fractions to units of micrometers, obtained by decomposition of iron carbonyls, has found wide application as the active component for magnetorheological liquids (MRLs) [1] that are suspensions of ferromagnetic particles in various liquid carrier media and reversibly change rheological behavior when a magnetic field is superimposed. Such liquid magnetizable systems capable of changing their characteristics under the influence of control signals in real time scale and of adapting to assigned conditions were given the name of "smart (intelligent) materials." At present, they are used as a basis for creating such promising pieces of equipment, as, for example, the technology of magnetorheological polishing [2], sealing elements [3], and dampers and position drives of electrohydraulic systems [4].

One of the main problems solved in the process of MRL synthesis using carbonyl iron is the improvement of their sedimentation stability, which is low due to the large difference in the densities of the dispersed phase and the dispersion medium and the limitations in the degree of size reduction of solid particles for the preservation of their macroscopic magnetic characteristics. Furthermore, the particles of carbonyl iron are not porous and their surface area coincides with the geometric one for spheres of appropriate size, while the surface itself has a low affinity with a bipolar organic substance, and, as a consequence, for relative stabilization of MRLs one has to introduce a rather great number of surface-active substances (surfactants). It should also be taken into account that the improvement in stability must not be accompanied by a considerable growth in the initial, without the influence of the magnetic field, viscosity whose magnitude must be minimized. This requirement flows out of the need to reduce the expenditure on pumping MRLs, on the one hand, and to increase the control range for rheological characteristics during the action of the magnetic field, on the other hand. The problem of decreasing the viscosity acquires a special significance in the case of using concentrated (40–50 vol.%) compositions, which are attractive from the point of view of manifesting a considerable magnetorheological effect. In this connection, the problem of improving the operating parameters of MRLs by developing methods of modification of the properties of carbonyl iron without a substantial change in its magnetic characteristics is rather topical, and its solution is the objective of this work.

Experimental. At present, there are methods for modification of the chemical properties of element iron, for example, the chemical inoculation of reactive groups, vitrification, microencapsulation into polymer envelopes, treatment with hydrogen for the removal of carbon and carbides, etc. [5, 6]. However, they are rather complicated and expensive, and to be used in MRLs, the most promising, from our point of view, appear

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[a]Academic Scientific Complex "A. V. Luikov Heat and Mass Transfer Institute," National Academy of Sciences of Belarus, Minsk, Belarus; [b]Institute of Physicoorganic Chemistry, National Academy of Sciences of Belarus, Minsk, Belarus. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 73, No. 3, pp. 476-481, May–June, 2000. Original article submitted June 3, 1999.

1062-0125/00/7303-0460$25.00

to be oxidizing treatment with the formation of a controlled quantity of ferromagnetic oxides in the surface layer: magnetite Fe_3O_4 or iron gamma-oxide Fe_2O_3. The presence of a thin oxide film on the surface of the particles enhances their specific adsorption of the hydrophilic part of the molecules of biphyllic surfactants. The following methods of oxidizing carbonyl iron powders have been tested: high-temperature (up to 510°C) treatment with water vapor at atmospheric pressure (method 1); hydrothermal (200°C) treatment under a pressure of 10 atm (method 2); soft vapor-air oxidation (method 3). Preliminary comparison showed that the first method is hard to control and requires the selection of conditions for each specimen batch; the second method is complicated and is also insufficiently reproducible. We chose the third method, which includes the following operations:

a) flotation of the most hydrophobic and fine particles with water (their quantity was at the level of 1–5 wt. %);

b) passivation of the surface by boiling in water for a short time to suppress pyrophorosity;

c) vapor-air treatment at a temperature not higher than 200°C.

In this work, three types of commercial specimens of carbonyl iron were used: grades R-10 (Russia), as well as S-1701 and S-3700 (USA).

Since we are dealing with particles of micron size and small degrees of transformation, the measurement of the depth of oxidation to calculate the thickness of the oxidized layer is a rather complex problem. Two methods have been worked out to determine the amount of the oxidized phase:

1) the gravimetric method, whereby the weighed sample was placed into a light aluminum sleeve connected to a torsion balance. The entire suspension was placed in a heated reactor with a system of hydrogen and helium feed. The specimens were pre-treated in a helium medium while being heated up to 600°C, and after reaching a constant weight and being cooled they were reduced in a hydrogen medium at a gradually increasing temperature;

2) the volumetric method based on the determination of the difference in the amount of hydrogen released in dissolving the starting and oxidized specimens. To achieve this, the specimen was introduced into a thermostatted vessel with 10% sulfuric acid, and the volume of the hydrogen released was measured with a gas burette with an equalizing bottle. To obtain reproducible results, it is necessary to have good wettability of the iron powder by an acid solution, which was attained by preliminary treatment of the iron with methanol.

As was mentioned, in carbonyl iron-based MRLs the stabilizers introduced are surfactants of various nature that are mainly derivatives of higher carboxylic acids, for example, glycerine monooleate or oleic acid itself. The nature of interaction between the iron particles and surfactants has noticeable effects on the properties of MRLs and is determined to a great extent by the condition of the surface oxide layer. Thus, the capacity of this layer with regard to surfactants is a most important characteristic of the MRL dispersed phase. At the same time, its determination with regard to specific surfactants entails certain experimental and methodological difficulties. In this connection, the most convenient way is to use a model adsorbant containing in its composition functional groups that have affinity with the surface of the oxidized particles of carbonyl iron. Experience shows that using methyl red (MR) with the application of the spectrophotometric method of measurement is optimum for this purpose. The procedure for determining the capacity by MR was as follows. A weighed iron sample (about 1 g) was filled with a known volume (usually 10 ml) of a solution of MR in benzene with a concentration of about $C = 10^{-2}$ g/liter and was thoroughly stirred. Samples of the liquid (about 0.5 ml) were taken at certain intervals of time and a SPECOL-11 spectrophotometer was used to measure the degree of absorption of monochrome radiation at a wavelength of $\lambda = 485$ nm, at which there is the maximum of the absorption of the benzene solution of MR. From the calibration plot constructed previously, we determined the concentration of MR in the solution and by it we calculated the adsorption A per unit mass of the specimen. In this manner, we can construct both the kinetic curves of MR absorption from solutions and the isotherms of adsorption.

Figure 1 shows an isotherm of MR adsorption on a carbonyl iron specimen that has been subjected to treatment in boiling water with subsequent drying at 200°C. It follows from the figure that the adsorption stops increasing at a residual MR concentration in the solution at the level of $2 \cdot 10^{-2}$ g/liter. The specific geometric

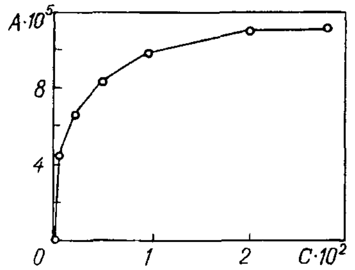


Fig. 1. Isotherm of the adsorption of methyl red at 20°C on carbonyl iron modified by method 3. *A*, g of MR/g of Fe; *C*, g/liter.

surface of the iron particles *q* evaluated by the assumed landing area of an MR molecule corresponds to the calculated one, as well as to the experimental magnitude, obtained upon the measurement of argon adsorption and having a value at the level of 1 m^2/g. Moreover, the magnitude of the oleic-acid adsorption immediately measured corresponds to the one by MR. Thus, the procedure of MR adsorption is suitable for the evaluation of the adsorption capacity of carbonyl-iron specimens, while for a comparative analysis it is sufficient to determine one kinetic curve of MR absorption from solutions with a starting concentration of $C \sim 10^{-2}$ g/liter.

To evaluate the influence of the surface modification process on the physical characteristics of carbonyl-iron particles, the methods of optical and scanning electron microscopy, x-ray phase analysis, and measurement of electrical conductivity were additionally used. Conductivity was measured in a cell with disk electrodes with the possibility of application of external pressure.

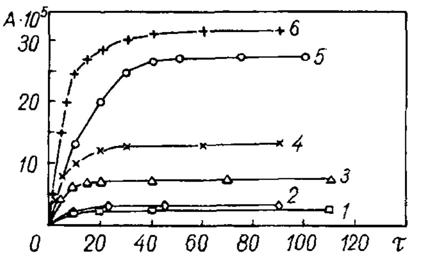
The MRL specimens were manufactured using a ball or a bead mill in a certain sequence. The required amount of carrier dispersion medium with surfactant additions was loaded into the mill; then a weighed iron powder sample was introduced into the liquid phase and the composition was intensely stirred for 2 h.

Measurements of the initial MRL viscosity were taken on a coaxially cylindrical Reotest-2 viscosimeter. The data on the influence of the field on the rheology of the specimens were obtained using a magnetorheometer based on a Rotovisco viscosimeter with a measuring cell of the "plate-to-plate" type. The sedimentation stability of the liquids was evaluated by the sedimentation constants $S_{sed} = u/g$ [7] measured on a specially developed device.

Results and Their Discussion. After the elutriation of the fine fraction, the carbonyl-iron particles of the P-10 and S-1701 series are almost regular spheres with an average size (diameter) of 3 μm. The percentage of particles 2–4 μm in diameter is less than 60%. The data were obtained based on the results of automatic scanning of microphotographs of specimens. The presence in the specimens of agglomerates with a diameter of less than 30 μm is due to the aggregation of particles 2–4 μm in diameter. The specimens of the S-3700 series are more finely divided: the average diameter of particles is about 1 μm. The specific surface measured by the argon adsorption is 0.9 m^2/g, which is close to the calculated *q* of nonporous spheres of the indicated diameter.

Within the resolution limits of the methods of optical and scanning electron microscopy no change in the particle shape and size was detected. However, the modification in soft conditions (method 3) leads to noticeable changes in the adsorption capacity of the specimens. The corresponding kinetic curves are given in Fig. 2. The experimental relationships show that the adsorption capacities of the specimens of initial iron R-10 and S-1701 are rather close (curves 1 and 2), which is understandable, if their close dispersion is taken into account. However, after treatment in boiling water (method 3) the capacity of R-10 iron grows by approximately a factor of three (curve 3), and the capacity of S-1701 iron increases by a factor of four (curve 4). Still higher is the adsorption capacity of modified iron S-3700, which is due to its higher dispersion (curve 6). A harder treatment of R-10 iron with water vapor in an autoclave (method 2) naturally leads to a deeper oxidation and capacity growth (curve 5). Thus, a modifying treatment of carbonyl iron under various conditions leads to an increase in its adsorption capacity due to surface oxidation.

A natural question is raised regarding the depth of the oxidized layer along the cross section of the microparticle and its chemical nature, taking into account the fact that new phases in these specimens were not detected roentgenographically (except for the specimens obtained in high-temperature water treatment – method



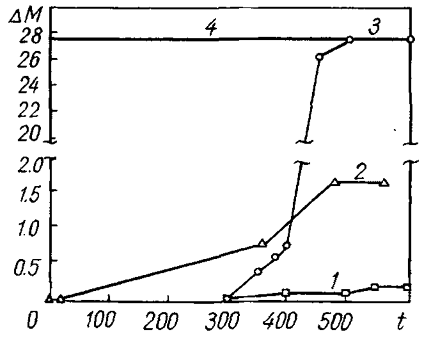
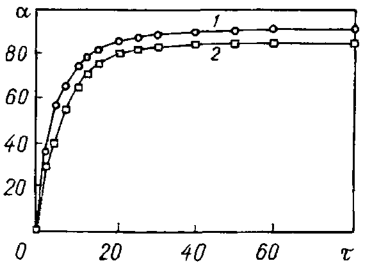


Fig. 2. Kinetic curves of the adsorption of methyl red at 20°C on carbonyl-iron specimens: 1) initial iron R-10; 2) initial iron S-1701; 3) R-10 iron modified by method 3; 4) same, S-1701; 5) R-10 iron modified by method 2; 6) S-3700 iron modified by method 3; τ, min.

Fig. 3. Decrease in the mass of carbonyl-iron specimens vs. temperature of reduction in hydrogen: 1) initial iron R-10; 2) R-10 iron modified by method 2; 3) magnetite (experiment); 4) magnetite (theory). ΔM, %; t, °C.



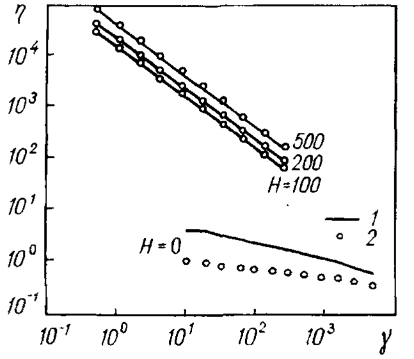


Fig. 4. Volume fraction of released hydrogen with respect to a theoretical one for pure iron vs. time of dissolution in sulfuric acid: 1) initial iron R-10; 2) R-10 iron modified by method 3.

Fig. 5. Viscosity vs. rate of shear with a variation of the magnetic field strength: 1) MRZh-1; 2) MRZh-2; η, Pa·sec; γ, sec^{-1}.

1). We were able to tackle this question in studying the process of reduction of different specimens of carbonyl iron. Figure 3 gives the change in mass as a function of the temperature for the initial iron R-10 and for the R-10 iron modified by method 3 and for the magnetite Fe_3O_4. A decrease in the mass for the magnetite agrees with the stoichiometric content of oxygen. The initial-iron mass remains practically constant. The agreement of the temperature intervals of reduction of the magnetic and the modified iron enables us to relate the mass decrease for the latter to the presence of about 6 wt.% of Fe_3O_4 in its composition. The results of studying the kinetics of acidic dissolution of iron confirm the conclusions on the oxidation depth obtained by the reduction method. Figure 4 presents the corresponding curves. A conversion of the difference in the amount of released hydrogen to iron oxide results in its content in the specimen's mass that is close to the content obtained by the previous method.

The presence of the oxide film on the surface is also demonstrated by the data on conductivity measurements. If the initial powder, without application of external pressure, has a conductivity at the level of the metallic one, the modified powder has a resistance of about 10^7 Ω·cm, and with a pressure increase to 100 atm the resistance decreases only by 2 orders of magnitude. This result is quite significant in terms of the use of carbonyl iron in the MRL composition since the presence of a low-conducting barrier at the points of contact of particles in formation of aggregated bridge structures in a magnetic field will prevent the induced currents from occurring. Simultaneously this indicates that the oxide layer on the surface of the iron particles is rather strong and fracture-resistant in the process of MRL preparation.

The investigated specimens of carbonyl iron were used to prepare experimental MRLs and to measure their magnetorheological characteristics. In particular, for comparative experiments, use was made of two MRLs that contained: carbonyl iron (48 wt.%), a dispersion medium based on pentaerythritol ester (49.7 wt.%), and a mixture of oxyphos (alkyl phosphate-based surfactant) and oleic acid (2.3 wt.%). We prepared MRZh-1 based on the initial carbonyl iron R-10 and MRZh-2 based on the R-10 iron modified by method 3. Figure 5 gives the results of measuring the initial viscosity (at $H = 0$) and the viscosities in the magnetic field with a strength of 100, 200, and 500 kA/m. It should be noted that the initial viscosity of the liquid based on the modified iron is severalfold lower than in the liquid based on the initial iron. The degree of increase in the viscosity of both specimens when the field is superimposed (the magnetorheological effect) remains unchanged. Furthermore, the sedimentation constant of 0.57 MSb in MRZh-2 (0.66 MSb in MRZh-1) also decreases. The given data demonstrate that the modified carbonyl iron adsorbs a great deal of the surfactant from the carrier medium due to the increased adsorption capacity of the oxide film on the particle surface. This contributes to an improvement in the sedimentation stability of an MRL and extends the control range of its rheological characteristics in the magnetic field by decreasing the initial viscosity.

Conclusions. The method proposed for modifying the adsorption properties of dispersed carbonyl iron, which involves a hydrothermal action of boiling water on the initial powder followed by vapor-air treatment at 200°C, is rather simple in realization, is reproducible, and leads to an improvement of the stability and characteristics of MRLs. The experiments showed that this procedure makes it possible to obtain concentrated MRLs with a high magnetorheological effect that are relatively stable and low-viscosity in the absence of a magnetic field. This substantially extends the control range for rheological characteristics of MRLs and, accordingly, the operating parameters of the devices and technological processes based on them.

NOTATION

C, concentration, g/liter; λ, wavelength, nm; A, adsorption (adsorption capacity), g of MR/g of Fe; q, specific surface of the particles, m^2/g; S_{sed}, sedimentation constant, stilbs; u, sedimentation rate of the particles, m/sec; g, acceleration of the gravitational or centrifugal force field, m/sec^2; τ, time, min; ΔM , relative mass decrease, %; t, temperature, °C; α, volume fraction of released hydrogen, %; H, magnetic field strength, A/m; η, dynamic viscosity, Pa·sec; γ, rate of shear, sec^{-1}.

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