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New methods for preparing mercury-based ferrofluids

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Metallic ferrofluids based on magnetic particles in mercury have been produced by two new methods. Alloy particles of Fe-B, Fe-Co-B, Fe-Ni-B, and Co-B were prepared by reduction of the transition metal ions in aqueous solutions by NaBH_4 and subsequently suspended in mercury. In one preparation, the metallic mercury was added to the solution with precipitates and in another method produced simultaneously with the precipitates by reduction of mercury ions to metallic mercury. The samples were characterized by magnetization and Mössbauer spectroscopy measurements.

INTRODUCTION

Ferrofluids are magnetic liquids that consist of ultra-small ferro- or ferrimagnetic particles suspended in a liquid carrier.^{1,2} The carrier liquid is typically an organic liquid or water and the magnetic particles are typically maghemite or magnetite. Metallic ferrofluids have the advantage that they are excellent electronic and heat conductors, which may be utilized in, e.g., heat exchangers and for more efficient cooling in rotating shafts.³

Metallic ferrofluids based on mercury as the carrier and small iron or cobalt particles in suspension have been studied for many years.^{4,5} Two methods have, up to now, been utilized for preparing these ferrofluids. One method has been to reduce transition metal ions in aqueous solution to the metallic state by using the reducing ability of sodium in sodium amalgam with simultaneous incorporation of the transition metal atom in the amalgam.⁴ The second method is to electroplate the transition metal ions into a mercury cathode under vigorous stirring.⁵ Ultra-small ferromagnetic particles are thereby formed.³⁻⁸ The particles have, in the case of iron, earlier been assumed to be α -Fe particles, but recent Mössbauer spectroscopy studies of such ferrofluids have revealed that probably metastable Fe-Hg alloy particles have been formed.^{6,8,9}

We report here on two new methods for preparing metallic ferrofluids. The ferrofluids are still based on mercury as the metallic carrier liquid and on reduction of transition metal ions to the metallic state, but the ions are now reduced to the metallic state by use of an alkali-metal borohydride in aqueous solution. The magnetic particles prepared by this method have diameters in the range 10–200 nm (Refs. 10–12) and they may be amorphous due to incorporation of boron during the reduction.¹¹⁻¹³ Magnetization and Mössbauer spectroscopy measurements have been used for studies of the prepared ferrofluids.

EXPERIMENT

In the first series of preparations (method A) Fe-B, Fe-Co-B, Fe-Ni-B, Co-B, and Ni-B particles were produced by dropwise addition of an aqueous solution of NaBH_4 (100 ml; 0.2 M) to an aqueous solution of transition metal ions (200 ml; 0.2 M). Five solutions with transition metal ions were prepared with the compositions: (1) 100% Fe; (2) 80% Fe, 20% Co; (3) 80% Fe, 20% Ni; (4) 100% Co; and (5) 100% Ni. The salts used were

FeSO_4 , CoCl_2 , and NiCl_2 . Black precipitates were formed and metallic mercury was then added to the slurry and mixed with the precipitates with the purpose to suspend the particles in the mercury.

Magnetization measurements on samples prepared by method A were performed at 295 K employing a conventional vibrating-sample magnetometer.

Two other preparations were performed with another method (method B) by which the iron ions were obtained by dissolving metallic iron in concentrated HCl. A mercury salt (HgCl_2) was then dissolved in the solution, whereafter drops of aqueous solutions of concentrated NaOH were added to obtain a pH of about 3 in the salt solutions. In the first preparation 12.5 ml of 0.2-M NaBH_4 in aqueous solution was added dropwise to 7.5 ml of 0.2-M salt solution (0.195-M Hg and 0.005-M Fe). A second preparation was also performed with Co ions in the salt solution. Here 17 ml of 0.2-M NaBH_4 in aqueous solution was added to 10 ml of 0.2-M salt solution (0.195-M Hg, 0.003-M Fe, and 0.002-M Co). By both preparations metallic mercury and a black precipitate were formed, which were then mixed to result in ferrofluids.

In method B the iron metal dissolved in HCl was 90% ^{57}Fe in order to make it possible to perform Mössbauer spectroscopy studies on the samples. These ferrofluids were made into thin films by squeezing a droplet of the ferrofluid and, subsequently, freezing the films in liquid nitrogen. The samples were studied at 12, 80, and 220 K by Mössbauer spectroscopy. The Mössbauer spectroscopy measurements were performed using a constant acceleration spectrometer with a ^{57}Co source in rhodium. The velocity scale was calibrated by measurements on a 12.5- μm α -Fe foil at 295 K. The isomer shifts are given relative to α -Fe at 295 K.

RESULTS AND DISCUSSION

It was found that the Fe-Ni-B, Co-B, and Ni-B particles prepared by method A were readily suspended in mercury. With increasing concentration of metal particles the produced amalgam changed from a liquid to a paste-like state. The viscosity could be decreased again by addition of mercury. The Fe-B and Fe-Co-B particles prepared by method A could not be suspended in mercury.

None of the precipitates entered the mercury if they were washed in distilled water prior to mixing with mer-

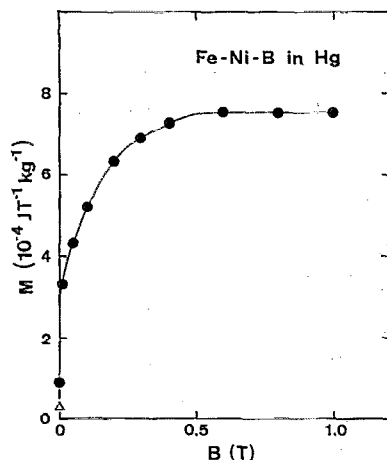


FIG. 1. Magnetization vs applied field for Fe-Ni-B in mercury. The measurements were performed at 295 K, starting with maximum applied field. The triangle shows the magnetization at zero field 5 min after the zero field was reached.

cury. The cause of this may be that the surface of the particles changed due to the rinsing with water, e.g., a thin oxide layer may have formed.

The Ni-B precipitate was the one that most readily mixed with the mercury, although both Ni and B are almost insoluble in mercury.¹⁴ The Ni-B were, so to say, "swallowed" by the mercury. Unfortunately, the black Ni-B precipitate was nonmagnetic. This is easily understood because amorphous Ni-B alloys with more than 20 at. % B have been found¹⁵ to have Curie temperatures below room temperature. Amorphous Fe-B, Fe-Co-B, and Fe-Ni-B alloys prepared by the reduction method employed in method A normally contain 20–40 at. % boron.^{10–12}

The suspension prepared with Fe-Ni-B and Co-B precipitates were, on the other hand, magnetic, i.e., metallic ferrofluids were produced. Indeed, Fe-Ni-B^{10,16} and Co-B¹² particles may be magnetic at room temperature even with high concentrations of boron in the matrix. Magnetic measurements were performed on these two latter ferrofluids with particle concentrations just below the critical concentration of rapidly increasing viscosity. The magnetization vs field curve obtained at 295 K for the Fe-Ni-B amalgam is shown in Fig. 1. The curve was measured by decreasing the applied field from 1.0 T to zero. The magnetization did not reach zero at zero field but a time dependence was found with the magnetization approaching zero. This shows that the particles probably have formed clusters or chains such that the particles feel resistance against rotation in the mercury. The magnetization vs field curve for the Co-B amalgam sample looked similar to that in Fig. 1.

The saturation magnetizations of the Fe-Ni-B and Co-B amalgam samples were found to be $7.5 \times 10^{-4} \text{ JT}^{-1} \text{ kg}^{-1}$ ($7.5 \times 10^{-4} \text{ emu/g}$) and $36.7 \times 10^{-4} \text{ JT}^{-1} \text{ kg}^{-1}$, respectively. Assuming the saturation magnetization for Fe, Co, and Ni to be 2.2-, 1.7-, and 0.6-Bohr magnetons, respectively, i.e., neglecting the influence of the boron and the mercury on the magnetic moments, the Fe-Ni-B and Co-B amalgam ferrofluids are estimated to contain approximately 0.4 and 2.3 wt. % magnetic particles, respectively. The critical concentration where the viscosity

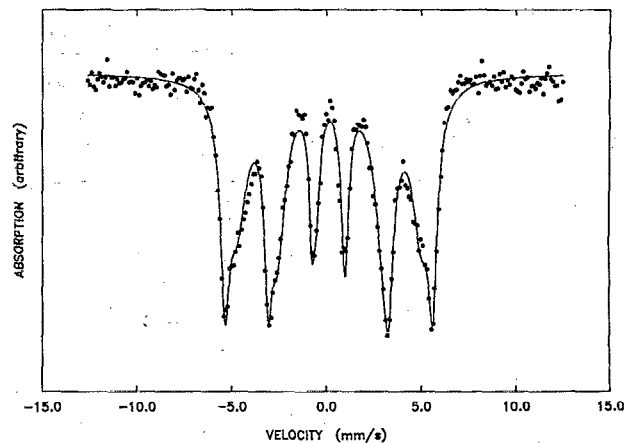


FIG. 2. Mössbauer spectrum, obtained at 80 K, for the Fe-B amalgam prepared by method B.

increases rapidly is for pure Fe particles in mercury around 1.0 wt. %.³

Mössbauer spectra, obtained at 80 K, of the ferrofluids prepared by method B, are shown in Figs. 2 and 3. Both spectra are seen to be magnetically split. The spectrum of the Fe-B amalgam (cf. Fig. 2) may be described by two sextets; one with sharp absorption lines, a magnetic hyperfine field of $34.1 \pm 0.5 \text{ T}$, an isomer shift of $0.12 \pm 0.03 \text{ mm s}^{-1}$, and constituting about 30% of the spectral area—and another sextet with broad absorption lines, a magnetic hyperfine field of $30.2 \pm 1.5 \text{ T}$ and an isomer shift of $0.19 \pm 0.03 \text{ mm s}^{-1}$. The former component is due to α -Fe, while the latter component may be ascribed to amorphous Fe-B. From the magnetic hyperfine field the boron content can be estimated to be about 10–15 at. %.¹⁷ The reason that the precipitate is partly crystalline in this case is probably that the pH varied between 3 and 9 during the reaction. When the precipitates are formed at pH values below 5 they have been reported to be partly crystalline and partly amorphous.¹⁸

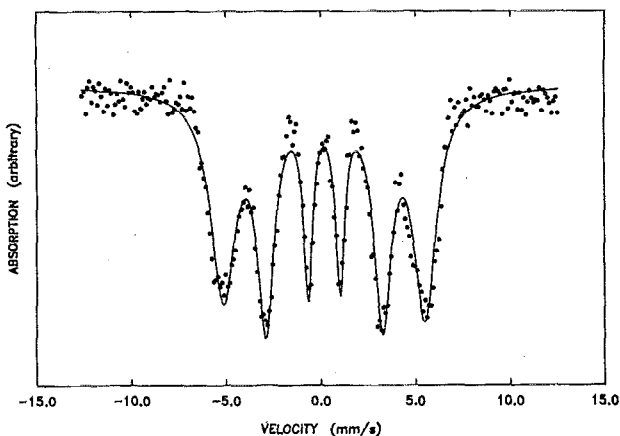


FIG. 3. Mössbauer spectrum, obtained at 80 K, for the Fe-Co-B amalgam prepared by method B.

The spectrum of the Fe-Co-B amalgam may be described by one sextet with broad lines with a magnetic hyperfine field of about 33.0 T, an isomer shift of 0.19 mm s⁻¹, and a negligible quadrupole shift. This component may be an Fe-Co alloy,¹⁹ but it may also be an Fe-Co-B alloy, possibly an amorphous alloy. The pH during the reaction has also for Fe-Co aqueous solutions been found to be important for the resulting composition and whether or not the precipitate become amorphous.²⁰

Measurements at 220 K showed slightly decreased magnetic hyperfine fields, while the measurements at 12 K yielded spectra very similar to those obtained at 80 K. It can therefore be concluded that the component with a hyperfine field of 38–40 T, obtained from measurements on Fe-Hg systems prepared by the conventional methods,^{6,8} is not present in the samples prepared by the method presented here. Hence the Fe seems not to have alloyed with the mercury.

CONCLUSIONS

Two new ways of producing metallic ferrofluids have been presented. The magnetic particles of Fe, Co, Ni, and B alloys were produced by reduction of the transition metal ions in aqueous solution by NaBH₄. Fe-B, Fe-Co-B, Fe-Ni-B, and Co-B amalgam ferrofluids were prepared by the methods. Also, Ni-B could easily be suspended in mercury but was nonmagnetic at room temperature. At least 2 wt. % magnetic particles could be suspended in the case of Co-B amalgams. The Fe-Hg alloy which is formed when amalgams have been prepared by more conventional means was not observed here.

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