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RESEARCH INTO THE PROPERTIES OF MAGNETIC FLUIDS PRODUCED BY MILLING TECHNOLOGY

BADANIA WŁAŚCIWOŚCI CIECZY MAGNETYCZNYCH WYTWORZONYCH W TECHNOLOGII MIELENIA

Key words: magnetic fluid, ferrofluid, magnetorheological fluid, micromilling, carbonyl iron.

Abstract: Magnetic fluids are substances with controllable rheological properties, containing nano- or micro- sized particles with magnetic properties suspended in a carrier fluid. The production of such fluids poses various challenges, but the critical issue is the fabrication of magnetically active particles of known size and required properties. They are usually produced using the 'bottom-up' method, where larger structures are formed during chemical synthesis and physical processes. This method is the most economical and practical in terms of efficiency, mainly when producing nanoparticles. The essence of the second method, 'top-down,' involves the fragmentation of the material, mainly through chemical-mechanical processes like milling. This method takes more time but does not involve the generation of environmentally harmful substances. It is characterized by simplicity and provides greater control over the sizes of the produced particles. The paper presents the results of research on the production of magnetic fluids based on carbonyl iron powder, which was fragmented using a planetary micro-mill. Powders differing in particle size and magnetic properties were considered. Oleic acid and oleoyl sarcosine were used as surfactants. Particle size and rheological properties of the obtained magnetic fluids were examined. The aim of the study was to determine the feasibility of producing magnetic fluids on a laboratory scale with designed physicochemical parameters. The research outcome is developing a procedure for obtaining a magnetic fluid that combines ferrofluid and magnetorheological fluid characteristics.

Słowa kluczowe: ciecz magnetyczna, ferrociecz, ciecz magnetoreologiczna, mikromielenie, żelazo karbonylkowe.

Streszczenie: Ciecze magnetyczne to substancje o sterowalnych właściwościach reologicznych, zawierające nano- lub mikrocząstki o właściwościach magnetycznych, zawieszone w cieczy. Problematyka wytwarzania tego typu cieczy obejmuje szereg wyzwań, jednak kluczowym zagadnieniem jest sposób wytwarzania aktywnych magnetycznie cząstek o znanym rozmiarze i wymaganych właściwościach. W większości przypadków wytwarzane są one metodą „bottom-up", czyli większe struktury powstają podczas syntezy chemicznej oraz przy pomocy procesów fizycznych. Jest to metoda najbardziej ekonomiczna i praktyczna ze względu na wydajność, szczególnie w przypadku wytwarzania nanocząstek. Istota drugiej metody „top-down" polega na rozdrabnianiu materiału, głównie za pomocą procesów chemiczno-mechanicznych jak mielenie. Wiąże się to z dłuższym czasem, ale metoda ta nie wiąże się z generowaniem szkodliwych dla środowiska substancji. Cechuje się ona prostotą oraz występuje większa możliwość kontroli rozmiarów wytwarzanych cząstek. W pracy przedstawiono wyniki badań dotyczących wytwarzania cieczy magnetycznych na bazie proszku żelaza karbonylkowego, który rozdrabniano z wykorzystaniem mikromłynka planetarnego. Wzięto pod uwagę proszki różniące się wielkością cząstek oraz właściwościami magnetycznymi. Jako surfaktant zastosowano kwas oleinowy oraz sarkozynian oleilowy. Zbadano wielkość cząstek oraz właściwości reologiczne otrzymanych cieczy magnetycznych. Celem pracy było określenie możliwości wytwarzania cieczy magnetycznych w skali laboratoryjnej o projektowanych parametrach fizykochemicznych. Rezultatem prac jest opracowanie procedury otrzymywania cieczy magnetycznej łączącej cechy ferrocieczy oraz cieczy magnetoreologicznej.

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INTRODUCTION

Magnetic fluids are suspensions of particles with magnetic properties in a carrier fluid and belong to materials with controllable properties. Due to a magnetic field's influence, there is a possibility of reversible, rapid change of rheological parameters or the flow direction. Depending on the size of the particles, two types of magnetic fluids can be classified: ferrofluid (FF), produced based on magnetic particles with a diameter of the order of nanometers (about 10 nm) **[L. 1]**, and magnetorheological fluids (MRF), in which particles with a size of micrometres (about 15 μm) are found **[L. 2]**. In order to prevent particles from aggregating, they are coated with a surfactant, which is most often a substance consisting of long-chain molecules of polar structure. The volume share of magnetic particles in a typical ferrofluid is about 7%, while that of magnetorheological fluids ranges from 20 to 50% **[L. 3]**. Therefore, ferrofluids are characterized by a smaller change in rheological parameters but higher stability of properties in a magnetic and gravitational field. Due to the differences in the characteristics of the two fluids, they are used in various applications. Ferrofluids are primarily used in seal construction, audio speakers as a lubricant, and in biomedical applications **[L. 4]**. On the other hand, magnetorheological fluids are used in vibration dampers, brakes, and clutches.

The properties of a magnetic fluid are a function of many parameters, in particular, the volume fraction of magnetic particles in the fluid, the magnetic properties of the particle material, the size and shape of the particles, and the type of carrier fluid. Stability, in turn, depends on the physicochemical properties and size of the particles and, above all, the internal energy of the fluid so that the particles do not sediment **[L. 5]**. The average particle size in magnetic fluids of about 10 nm can be considered a threshold size for inhibiting the agglomeration of magnetic fluid particles. Therefore, magnetorheological fluids are not stable fluids.

Ferrofluids are produced mainly by the 'bottom-up' method; larger structures are formed during chemical synthesis and physical processes. This is the most economical and practical method due to its efficiency. Magnetite-based ferrofluid (Fe_3O_4) can be produced by condensation, where the size of the particles depends primarily on the conditions under which the process occurs **[L. 6]**. The main procedure begins with co-precipitation of Fe (II) and Fe (III) ions with the addition of concentrated NH_4OH. The sludge is then isolated by magnetic decantation and treated with oleic acid during heating. Then, an organic carrier liquid is added with intense stirring. Procedures such as phase separation and excess surfactant and solvent extraction are often necessary to obtain concentrated magnetic fluids. The procedure thus requires specialized equipment and precise control of the conditions under which chemical reactions occur.

The second 'top-down' method of producing ferrofluid nanoparticles means that a smaller material is obtained mainly by chemical-mechanical processes like grinding from a larger material. In this case, the powdered material is placed into a mill, which is crushed between grinding elements. The main disadvantages of this process are that it takes longer and is more energy-intensive. The advantages are no harmful substances to the environment during production, and there is simpler control of particle size during the process, e.g., by changing the rotation speed. The grinding process is also characterized by the particles having higher magnetic saturation values **[L. 7]**.

The first attempts to produce ferrofluid by this method took three months. Through the development of this technology, especially the planetary micro-mill, the grinding process is much faster because of the high-energy impacts of grinding balls. This is possible because the grinding bowl, containing the material and grinding balls, rotates around the central axis, while the bowl with the material rotates in the opposite direction. Various powders with magnetic properties are used as input materials. An example is the process of grinding hematite (Fe_2O_3) discussed in the publication **[L. 8]**. An input material with an average size of 253 nm was used, and a minimum crystallite size of 17.1 nm was obtained for grinding at 600 rpm for 10 h. Much weaker magnetic properties than magnetite characterize hematite. There is a method of producing magnetite from hematite **[L. 9]**, but iron, which reacts with water, is often used for this purpose. In the work **[L. 10]**, nanoparticles with a size of 12 nm were obtained during milling for 97 h at a speed of 200 rpm. The synthesis of magnetite nanoparticles for hyperthermia is presented in **[L. 11]**. In this case, at a speed of 400 rpm for about 40 h of grinding first in water and then 12 h in hexane with oleic acid, particles with a size of 22 nm were obtained.

Producing magnetorheological fluids can be viewed as an intermediate method between the two discussed above. In this case, the input product is carbonyl iron. The preparation of fluids is based on mixing a powder together with suitable additives such as dispersing agents, antioxidants, thixotropic additives, or thickeners **[L. 12]**. Silica-based agents are common additives that stabilize and reduce sedimentation **[L. 13]**.

This paper presents the results of a study of the properties of magnetic fluids produced in a planetary mircomill. The initial product is a magnetic fluid composed of solid particles with sizes intermediate between those typical of ferrofluid and MR fluid.

MATERIALS AND METHODS

The fluids were obtained using a planetary miromill (PULVERISETTE 7 premium line). The input material was carbonyl iron powder, which reacted with water according to the following relation:

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$

The output product is magnetite, which creates a magnetic fluid, and hydrogen is a by-product. The mass of the input material was 1 g of iron, which yields 4.14 g of magnetite with a water requirement of 0.43 g. In the grinding process, due to the need to grind the material, the mass of water was higher, at 1 g. Carbonyl iron powders (CIP) supplied by BASF were used as input materials. The labelling and properties are shown in **Table 1**. OS and CC powders have a similar diameter range but different magnetic hardness. CC and CM powders, on the other hand, have similar hardness but different diameter ranges. By soft or hard material type, we should understand their magnetic properties. Magnetically hard materials are characterized by their high ability to maintain permanent magnetism and are difficult to demagnetize, as in the case of a permanent magnet. Soft materials are characterized by their ability to be easily magnetized but lose their magnetization as the magnetic field decreases.

Two compounds were chosen as the surfactant. The first is oleic acid $C_{18}H_{34}O_2$. This is the most commonly used compound for magnetic fluids. The chain length, in this case, is 2.772 nm. The second is oleoyl sarcosine, a fatty acid consisting of oleic acid and sarcosine ($C_{20}H_{39}NO_3$). The trade name of this substance is Perlastan O. It is a naturally occurring substance that exhibits various biological activities, such as antimicrobial and anti-inflammatory effects. It is also used in cosmetics and personal care products for its moisturizing properties. The chain length, in this case, is 3.08 nm. During grinding, the weight ratio of the bearing balls to the powder was 90:1, and the speed was 650 rpm. The powder was milled for 40 hours. Then, 3 ml of kerosene and 0.5 ml of surfactant were added. The amount was based on the recommendations described in the paper **[L. 14]**. Grinding under these conditions continued for another 12 h. Then 2.5 ml of base oil, designated SN100, was added, stirring the mixture for 2 h. Six magnetic fluids were produced, and the samples are summarized in **Table 2**.

Table 1. Properties of CIP powders
Tabela 1. Właściwości proszków CIP

Labelling	Fe iron content Fe,%	Diameter range, µm	Type
OS	Min. 97.5	3.4–4.4	Hard
CC	Min. 99.5	3.8–5.3	Soft
CM	Min. 99.5	7–9.5	Soft

Table 2. Designations of the produced magnetic fluid samples
Tabela 2. Oznaczenia wytworzonych próbek cieczy magnetycznych

Carbonyl Iron Powder (CIP)	Olein Acid (OA)	Perlastan O (PO)
CC	CC_OA	CC_PO
CM	CM_OA	CM_PO
OS	OS_OA	OS_PO

The produced magnetic fluids were subjected to two types of tests. The size distribution of the magnetic particles produced during the milling process was measured in the first stage. For this purpose, the Dynamic Light Scattering (DLS) method was used. In addition, rheological tests were conducted to determine the reaction of the produced fluids to the magnetic field. The property measurements were carried out at least a week after the samples were produced due to the need to evaporate excess kerosene. After manufacture, the fluids had a consistency similar to plastic grease. However, they showed greater stability than typical magnetorheological fluids (without a clear separation of the particles from the carrier liquid). **Figure 1** shows an example of two samples of the fluids about six months after their manufacture.

Fig. 1. Photograph of the magnetic fluids produced
Rys. 1. Fotografia wytworzonych cieczy magnetycznych

STUDIES OF PARTICLE SIZE RIBUTION

The measurements were carried out at a temperature of 25°C. **Fig. 2** shows the results of measuring the diameter distribution as a number-weighted distribution (a) and a volume-weighted distribution (b). The number-weighted distribution corresponds to results obtained on a microscope, such as TEM, and will give an equal representation of small and large particles. A volume-weighted distribution corresponds to results obtained from laser diffraction or X-ray diffraction and will be more sensitive to the presence of larger particles. The results of the average particle size measurement are summarized in **Tab. 3**.

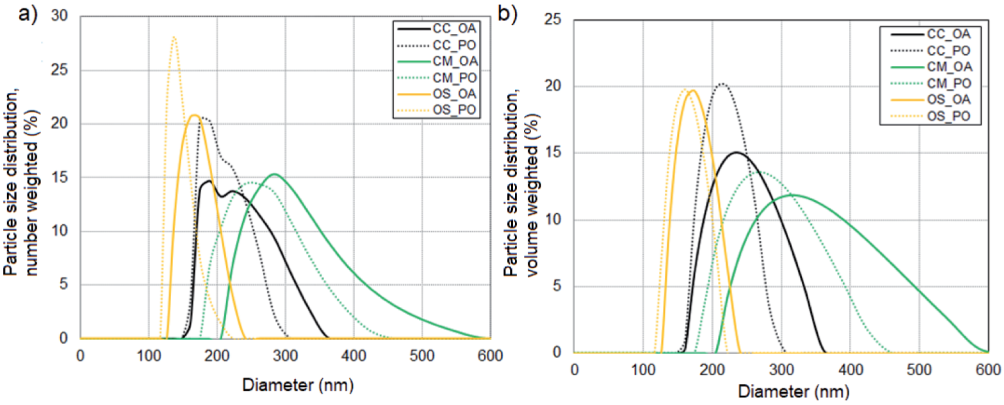

Fig. 2. Particle size distribution: a) number-weighted distribution, b) volume-weighted distribution
Rys. 2. Rozkład wielkości cząstek: a) rozkład ważony liczbowo, b) ważony objętościowo

Table 3. Average particle size
Tabela 3. Zestawienie średnich wielkości cząstek

Sample	Average particle diameter distribution	
	Number-weighted	Volume-weighted
	nm	nm
CC_OA	204	240
CC_PO	148	221
CM_OA	282	306
CM_PO	240	260
OS_OA	174	174
OS_PO	116	160

RHEOLOGICAL STUDIES

Rheological properties were measured on an MCR 301 rotational rheometer (Anton Paar) using a measurement geometry of parallel plates with a diameter of 20 mm. The rheometer was equipped with a module (MRD-180/1T), which allows measurements to be carried out in a magnetic field. The tests were performed at a constant temperature of 25°C. Two types of tests were performed: measured viscosity of magnetic fluids without magnetic field at increasing shear rate and measured viscosity at linearly increasing value of magnetic field induction and at constant shear rate. Each measurement was repeated at least twice.

In **Fig. 3**, the flow curves of the magnetic fluids produced are shown. In all cases, the non-Newtonian behavior of the samples was observed, indicating that shear thinning may be present, which is a typical behavior of magnetic fluids. Apparent differences in the behavior of the fluids due to the type of surfactant used can be seen.

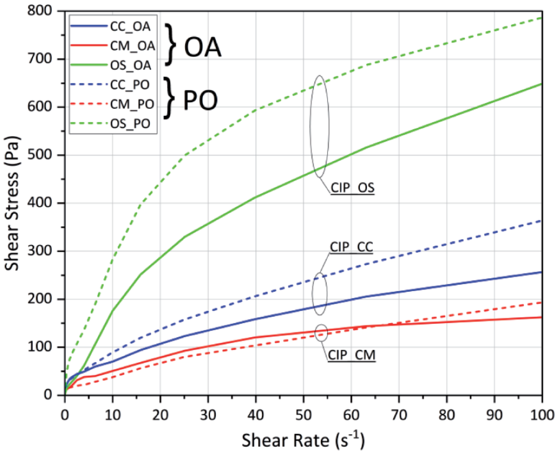

Fig. 3. Flow curves of the fluid samples prepared under zero magnetic field conditions

Rys. 3. Krzywe płynięcia wytworzonych cieczy wyznaczone w warunkach zerowego pola magnetycznego

Fig. 4 shows the results of dynamic viscosity measurements of the magnetic fluids that were produced. All results refer to conditions of no magnetic field, temperature of 25°C, and shear rate of 100 s^{-1}. Despite the complexity of the process and the variety of feedstock materials, similar values of zero-state viscosity were obtained. It is notable that the results received can be divided into three groups due to the CIP powder used. The highest viscosity values were obtained for the fluid produced based on the OS powder, while the lowest values were obtained for the CM powder.

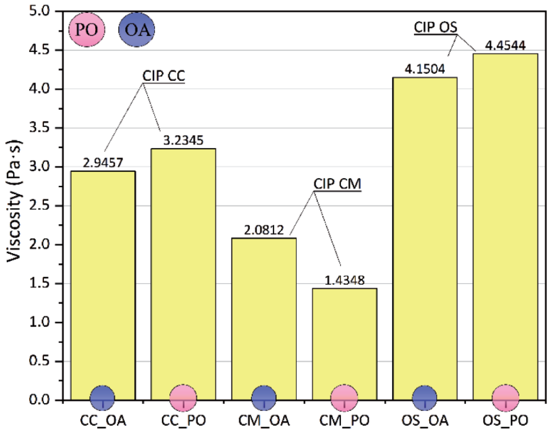

Fig. 4. Dynamic viscosity of the FF samples prepared

Rys. 4. Lepkość dynamiczna wytworzonych próbek cieczy magnetycznych

In the next stage, tests were performed on the effect of magnetic field values on the dynamic viscosity of the fluids prepared (**Fig. 5**). In this case, the results can be divided into different groups due to the CIP powder used (magnetically hard and soft) and the size of the feedstock diameter. The highest viscosity values were obtained for fluids obtained from CC and CM powders, i.e. the soft type.

It is worth noting that significant differences were observed depending on the surfactant used. In the case of the CC and CM powders, higher values were obtained for the Perlastan O surfactant, which may be related to the higher chain length than in the case of oleic acid. This affects the more significant value of the hydrodynamic diameter of the particles and, thus, the higher increase in viscosity. The smallest values were obtained for the hard-type OS material. Whereby in this case, higher viscosity values were obtained for oleic acid. This may be because there is an almost 28% proportion of particles with a diameter of about 136 nm for Perlastan O, and the oleic acid fluid has a higher proportion of particles with a larger diameter.

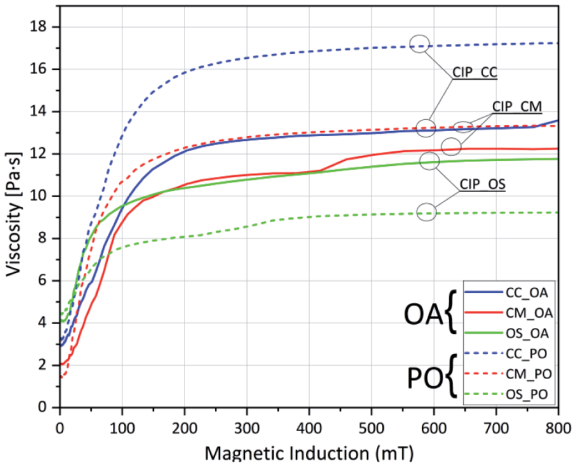

Fig. 5. Dynamic viscosity vs. magnetic field induction

Rys. 5. Lepkość dynamiczna w funkcji indukcji pola magnetycznego

To better illustrate the magnetorheological effect, **Fig. 6** shows the values of relative viscosity change. The viscosity increment ranges from about 2 to more than 9. For typical ferrofluids, the viscosity nearly doubles, and for magnetorheological fluids, it increases approx. 1,000 times **[L. 15]**. This indicates that the prepared fluids are more similar to ferrofluids in terms of viscosity increase and particle size.

The stronger magnetorheological effect may result from the higher value of particle magnetization or it may indicate the presence of magnetic particles of larger sizes. The largest values were obtained for CM, CC, and OS powders, respectively, which are consistent with the diameter size.

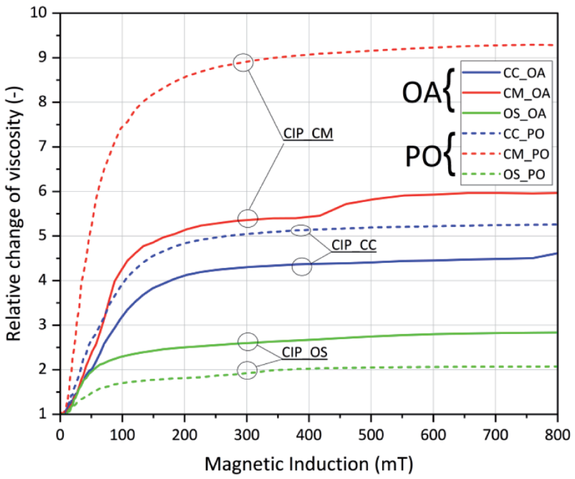

Fig. 6. Relative change in dynamic viscosity

Rys. 6. Względna zmiana lepkości dynamicznej

CONCLUSIONS

The paper presents the results of preliminary work on the fabrication of magnetic fluids based on carbonyl iron powder by milling. The main conclusions of the work are as follows:

- Planetary micromill technology can grind carbonyl iron to particle sizes in the order of tens of nanometers.
- The type of surfactant used significantly affects the behavior of the fabricated magnetic fluids. In the case of oleic acid and Perlastan O, both succeeded in producing sedimentation-stable magnetic fluids.
- The CC and CM powders are the most suitable for further work due to the strongest magnetorheological effect, i.e., the highest change in viscosity of these samples when a magnetic field is applied.
- Further research is needed to increase the repeatability of the process.

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