MAGNETIC FLUIDS AND APPLICATIONS HANDBOOK

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PREFACE

Magnetic Fluids are a new class of engineering materials. They were discovered approximately 30 years ago and have progressively become a technological material very useful for many engineering application.

An International team of the best specialists in the field is being assembled by UNESCO to prepare a handbook "Magnetic Fluids and Application", in order to provide a base for engineers to get acquainted with this new technological material. The project being undertaken within the UNESCO programme "Series of Learning Materials and Engineering Sciences".

The handbook presents a state of the art information and is edited by a board of 10 prominent specialists in the field. It draws on contributions from 28 experts from every substantial branch of magnetic fluids theory and applications. This volume is organized around modern methodology and the kind of problems and issues deal with the contemporary engineers. It gives practical useful data on critical recent topics. The book provides quick acess to material data, practical design rules and techniques, marthematics and ready to use formulas. It also give for a non-expert an elementary grasp of the subject.

B.Berkovski

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INTRODUCTION,

by B.Berkovski

Magnetic fluids are a new class of engineering materials. With the coexistence of magnetic and liquid properties, magnetic fluids provide opportunities to create innovative products and solve complex technical problems. To date, the materials have been used for engineering solutions in such diversified industries as semiconductor, audio, bearing, damping, medical and instrumentation. The scope of applications, however, is much greater and one envisions a rapid growth both in basic research and commercial products.

The objective of this handbook is to provide a working guide to magnetic fluids. Several books have been written on the subject of magnetic fluids but these books assume a graduate level engineering/science education for reader. Therefore, these books are of limited use for practicing engineers in industrial environments who are seeking a rapid working knowledge of this area, and to beginning students who are interested in entering this field.

In the handbook, the concepts and basic principles have been explained in a simple manner, but the significance fully described; and sufficient examples are presented in regard to the use of the theory in practical situations. The liquid and magnetic phenomena, the core of magnetic fluid technology, are described in an easy-to-understand format. The fundamental characteristics of magnetic fluids along with measurement techniques are discussed. The design and operational principles of magnetic fluid devices are explained in detail with a view towards assisting the user with an in-depth understanding of the technology.

The handbook is user friendly. Magnetic fluids and related topics are presented in such a manner that the engineer quickly learns about this field and becomes effective in the use of the technology. Students in the academics should also find the book to be valuable because of its basic nature and broad subject matter.

LIST OF MAIN SYMBOLS

x, y, z -Cartesian coordinates
r,φ, z -cylindrical coordinates
t-time
ω - frequency
$\vec{k}$ - wave vector
R_1, R_2 - main radii of surface curvature
$\vec{n}$ - external normal vector to a surface
ρ - density
P - pressure
T - temperature
$\vec{v}$ - velocity
$\vec{q}$ -specific heat flux
$\vec{H}$ - magnetic field intensity
$\vec{B}$ - magnetic field induction
$\vec{M}$-magnetization (magnetic moment of unit volume of the medium)
μ_0-magnetic permeability of vacuum
χ - magnetic susceptibility ($\vec{M} = \chi\vec{H}$)
μ - magnetic permeability of medium ($\mu = \mu_0(1+\chi)$)
η - dynamic viscosity coefficient
ν - kinematic viscosity coefficient ($\nu = \eta/\rho$)
C - heat capacity
λ - thermal conductivity
κ - thermal diffusivity ($\kappa = \lambda/\rho C$)
σ - surface tension coefficient
k - Boltzmann's constant
$\vec{g}$ - gravity acceleration
$\beta_\rho = -(1/\rho)(\partial\rho/\partial T)$ - relative temperature density coefficent
$\beta_M = -dM/dT$ - absolute temperature magnetization coefficient
$\beta_\sigma = -d\sigma/dT$ - absolute temperature surface tension coefficient
l - characteristic dimension
$\vec{G}$ - characteristic gradient of magnetic field intensity
$\vec{\gamma}$ - characteristic temperature gradient
δ_{ik} -Kronecker symbol
ε_{ikl} - Levi-Civita symbol

DIMENSIONLESS NUMBERS

$\mathrm{Re} = vl/\nu$ - Reynolds number
$\mathrm{We} = \rho v^2 l/\sigma$ - Weber number
$\mathrm{Bo} = \rho g l^2/\sigma$ - Bond number
$\mathrm{Bo}_m = \mu_0 M G l^2/\sigma$ - magnetic Bond number
$\mathrm{Gr} = \beta_\rho g\gamma l^4/\nu^2$ - Grashof number
$\mathrm{Gr}_m = \mu_0\beta_m G\gamma l^4/\rho\nu^2$ - magnetic Grashof number
$\mathrm{Pr} = \nu/\kappa$ - Prandtl number
$\mathrm{Ra} = \mathrm{GrPr}$ - Rayleigh number

$\mathrm{Ma} = \beta_\sigma \gamma l^2/\eta\kappa$ - Marangoni number
$\mathrm{Pe} = \mathrm{RePr}$ - Peclet number
$\mathrm{Nu} = ql/\lambda\Delta T$ - Nusselt number

$$\left.\begin{array}{l} \mathrm{S} = \mu_0 M^2 l/\sigma \\ \mathrm{Si} = \mu_0 M^2/\sqrt{\rho g \sigma} = \mathrm{S}/\sqrt{\mathrm{Bo}} \end{array}\right\} \quad - \text{magnetic fluid interface numbers}$$

NOTATION OF TRIGONOMETRIC FUNCTIONS

sin-(sine)
cosin-(cosine)
tg-tan-(tangent)
ctg-cotan-(cotangent)
sh-sinh-(hyperbolic sine)
ch-cosh-(hyperbolic cosine)
th-tanh-(hyperbolic tangent)
cth-coth-(hyperbolic cotangent)

CHAPTER 1

PHYSICO-CHEMISTRY OF MAGNETIC FLUIDS: PREPARATION AND PROPERTIES

Editors:

V.Cabuil,

S.Charles,

R.Massart

Chapter 1

PHYSICO-CHEMISTRY OF MAGNETIC FLUIDS: PREPARATION AND PROPERTIES

Editors: V.Cabuil, S.Charles, and R.Massart

1.1 INTRODUCTION, *by S. Charles*

Intrinsic liquid 'ferromagnets' are not known to exist although theories have been proposed that suggest there is no inherent reason why they should not exist [1,2]. All known ferro- and ferri- magnetic materials undergo a change to a weakly magnetic state (paramagnetic) at a temperature called the Curie temperature which is below that of the melting point of the material e.g. for iron, the Curie temperature is 770°C and the melting point is 1535°C.

The term magnetic fluid is, in this handbook, used to denote both magnetic colloids and non-colloidal suspensions (magnetorheological fluids).

Magnetic colloids (magnetic fluids) are defined as very stable colloidal suspension of ultrafine particles (~10 nm) of ferro - and ferri - magnetic materials in carrier liquids such as hydrocarbons, esters, etc. These fluids have the usual properties of liquids but in addition behave in a manner expected of an intrinsic liquid ferromagnet, ie they move as a whole in the direction of highest magnetic field and retain their liquid properties in the most intense magnetic fields. The study of magnetic colloids as we know them today started in 1965 through the pioneering work of Papell [3] and Rosensweig [4], although magnetic colloids were prepared by Elmore in 1938 to detect magnetic domains at the surface of a metal by the Bitter technique. Bitter fluid does not have the stability of an ultra stable colloid since detection of domains depends on concentration of the magnetic particles at the domain boundaries, where the magnetic intensity is greatest.

Non-colloidal magnetic suspensions (magnetorheological fluids) contain micron-sized particles and are analogous to electrorheological fluids which respond to an electric field rather than a magnetic one. Magnetorheological fluids differ in one major respect form magnetic colloids in that they undergo large changes in their rheological properties, eg. a liquid to solid transition, when exposed to a modest magnetic field, ie. they are not stable in the presence of a magnetic field.

In the case of magnetic colloids, the particles used in most commercial application are of iron oxides (magnetite, berthollide or maghemite) because of

their resistance to oxidation, rather than the transition metals which have the benefit of higher saturation magnetisation. For non-aqueous dispersions the particles are coated with surfactants to overcome van der Waals forces of attraction. The particles (~10 nm) are sufficiently small that Brownian motion is sufficient to maintain them in a stable dispersion. However in the case of magnetorheological fluids, where micron-sized particles are used, benefit can be made of the higher magnetisation of the transition metals because oxidation is not a serious problem. Further, because of the large size of the particles and their high density ($\sim 8 \times 10^3$ kgm^{-3}) compared with the supporting liquid, Brownian motion, is insufficient to prevent sedimentation and thus other methods have to be relied upon, eg, additives have been used to produce a reversible thixotropic transformation.

Magnetic colloids have been used commercially for a number of years in numerous devices, such as rotating shaft seals and exclusion seals, loud speakers, dampers, inclinometers etc, whereas magnetorheological fluids have achieved commercial use in hydraulical devices, loudspeakers and in grinding applications, mainly in the former USSR.

Numerous patents (~1000) and scientific papers (~2000) have been published related to the preparation, properties and application of magnetic fluids [5,6,7,8].

1.2 PARTICLES SUITABLE FOR MAGNETIC COLLOIDS,

by S.Charles and R. Massart

1.2.1 Which Magnetic Materials are Suitable for Magnetic Fluids?

In Fig. 1.1 five different types of magnetism are represented which are referred to in various sections of this handbook. From the point of view of magnetically strong fluids one can ignore diamagnetism, paramagnetism and antiferromagnetism, although one should be aware of their existence. Only ferromagnetism and ferrimagnetism need be of concern here, although the role of diamagnetism is important in the discussion of magnetic composites. A thorough understanding of the origins of ferro - and ferrimagnetism need not be of concern in this handbook except to say that the first theories of ferromagnetism were proposed by Heisenberg in 1928 on the basis of the newly-developed quantum theory. In this theory a quantum-mechanical exchange interaction occurs between spins of adjacent atoms leading, in the case of parallel spins, to ferromagnetism.

Associated with each spin is a magnet moment and it is the magnetic moment per unit volume of material which defines M_s. M_s has the SI units, Am^{-1} (amperes per metre). (See section on units and definitions). In ferro- and ferrimagnetic materials the spontaneous ordering of spins disappears at the Curie temperature as illustrated in Fig. 1.2. In this Fig., the saturation magnetisation $M_s(T)$, which is the basic quantity characterising any magnet

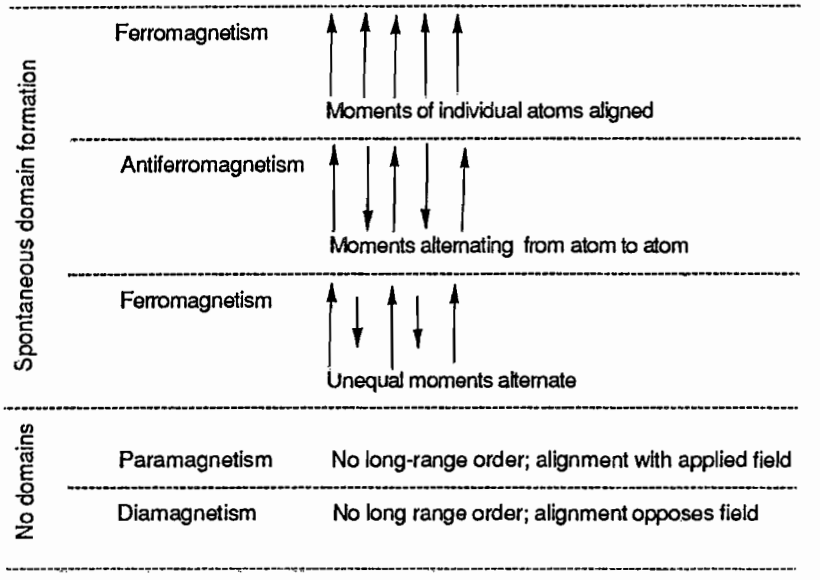

Figure 1.1. Five different types of magnetism.

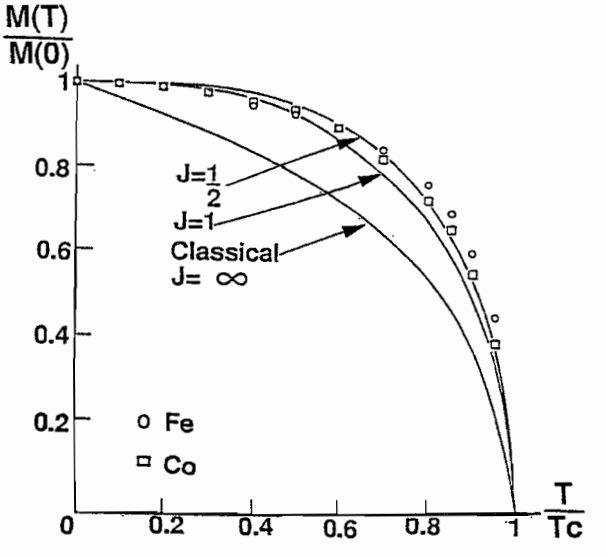

Figure 1.2. Saturation magnetization as a function of temperature.

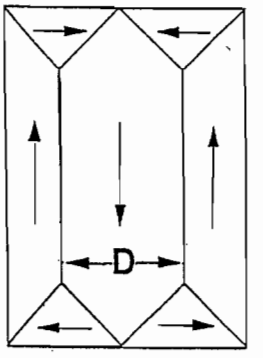

Figure 1.3. Magnetic domains of cubic material.

is shown as a function of temperature. For antiferromagnetic materials, no net moment is observed at any temperature.

If all the spins in a piece of magnetic material were aligned, then this piece of material would be permanently saturated and possess a large moment with a resulting large magnetostatic energy due to the 'free' magnetic poles formed on the surface. This is not the usual case in nature, and it was not until Weiss in 1907 proposed his theory of a domain structure that this apparent contradiction was resolved. Thus in the absence of an applied magnetic field, the magnetic structure of ferro- and ferrimagnetic material consists of domains, the magnetization vectors of which are oriented so as to minimize the magnetostatic energy, as shown in Fig. 1.3. Each of the domains consists of aligned spins. In addition, in the absence of an applied magnetic field, the magnetic vector of a single domain will align along a particular crystallographic 'easy axis'. It is an intrinsic effect determined by spin-orbit coupling between adjacent spins, which in turn determines which of the crystal axes are 'easy-axes' of magnetization. In the case of magnetite which has an inverse spinel structure, the easy axis is the cube edge and for bulk cobalt at room temperature, it is the hexagonal axis. The magnitude of the energy needed to move the magnetization vector from its easy direction to some other direction is determined by the magnetocrystalline anisotropy constants, given by the symbol K. The units of K are Jm^{-3}.

Table 1.1 contains a list of typical ferro- and ferrimagnetic materials and their properties. The most commonly used magnetic material used as the basis of magnetic colloids in most present day applications is iron oxide (magnetite Fe_3O_4, berthollide (partially oxidised magnetite), or maghemite -Fe_2O_3) and for magnetorheological fluids, the transition metals and alloys. Magnetic colloids are often stated as containing magnetite but almost invariably some oxidation has taken place. Fortunately the transition from magnetite to γ-Fe_2O_3 does not lead to a significant reduction in saturation magnetization. The magnetocrystalline anisotropy of magnetite is sufficiently low that any significant

Table 1.1. Magnetic data

Substance $MO.Fe_2O_3$	Lattice parameter (nm)	M (kAm^{-1}) (298 K)	Tc K	Anisotropy constants, (298 K), ($\times 10^{-3}$ Jm^{-3})	
				K_1	K_2
Mn	0.85 (is)	400	573	-3	
Fe	0.84 (is)	484	858	-11	
Co	0.84 (is)	425	793	200	
Ni	0.83 (is)	270	858	-6.2	
Cu	(a = 0.82 (tet) (c = 0.87	135	728		
Mg	0.84 (is)	120	713	-2.5	
$Ba_{0.6}Fe_2O_3$	(a = 0.59 (hex) (c = 2.32	380	723	300	
Fe_2O_3 - Fe_3O_4 (Berthollide)	(is)		863	-3	
γ-Fe_2O_3	8.33‡	414	863	-4.6	
Fe(α)	0.286 (bcc)	1707	1043	48	20
Co(α)	(= 0.25 (hcp) (c = 0.41	1400	1404†	450	150
Ni	0.35 (fcc)	485	631	-50	-2
Gd	(a = 0.36 (hcp) (c = 0.58	1980	293	20	-0

KEY

† Co(α) undergoes transformation to fcc Co(β) at 733 K. However the structure of small Co particles (<10 nm) at 290 K is generally fcc.

‡ defect spinel

(is) inverse spinel/cubic

elongation or deviation from sphericity produces an enhanced anisotropy due to shape. This will be discussed in section 1.7.1.1.

In general, in most applications the magnetic properties other than saturation magnetization M_s is of little consequence.

However, there are some less well developed application of magnetic colloids e.g. ink-jet magnetic inks, heat exchangers etc. where properties other than the saturation magnetisation are of importance. The role of these properties will also considered in section 1.7.1.1.

The great advantage of the ferrites is that they are oxides and provided that the operating temperatures are not too high (< 200°C) then they should remain strongly magnetic for the expected lifetime of the device in which they are used. However, the great disadvantage of ferrites is their relatively low saturation magnetization. The maximum fluid saturation magnetization that can be attained for a magnetic colloid with acceptable viscosity is not much greater than 100 kAm^{-1} (1200 Gauss).

In theory magnetic fluids with much higher magnetization are attainable by using particles of the transition metals/alloys or rare earth metals. As can be seen in table 1.1, the saturation magnetization of Fe is approximately three times that of most ferrites. Unfortunately all metals, particularly in the form of small particles (< 10 nm) found in magnetic colloids suffer rapid oxidation. However particles of < 10nm diameter dispersed in hydrocarbons

and esters have been made oxidatively stable at room temperature over long periods (years) by appropriate choice of a coating agent, such as a surfactant. However even at temperatures as low as 50°C, such particles still oxidise rapidly. Since in most applications there is an element of heating, there seems little prospect of metal particles produced by existing methods being employed in magnetic colloids for the present day commercial applications. The problem of oxidation of micro-sized particles used in magnetorheological fluids is however not so acute because the surface area of volume is so much smaller for these particles.

The various methods of preparation of small magnetic particles (< 10nm diameter) may be conveniently described under the following headings. Details of the dispersions of such particles are given in Section 1.4 and detailed typical examples of the preparation of magnetic colloids given in Section 1.10.

1.2.2 Ferrites

Wet-grinding

Wet grinding of ferrites to produce small particles (~10nm) suitable for use in magnetic colloids was discovered by Papell in 1965, and has since been investigated by many other workers (see published bibliographies [5,6,7,8]. The method consists of ball-milling micron-sized particles of ferrite, in the presence of a suitable surfactant acting as a grinding aid and a carrier, until the ferrite is in the colloidal state i.e the particles are $\leq$ 10 nm in diameter. This process usually takes a long time, of the order of 1000 hours. The role of the surfactant is to prevent agglomeration and the quantity used in the mill corresponds approximately to a monolayer coating on the particles. A typical composition in the ball-mill consists of ~4% by volume of ferrite, 10-20% by volume of surfactant and the rest of carrier solvent.

This method does not have the speed of production to be found using chemical precipitation methods nor is it suitable for metals because the materials need to be brittle.

Chemical precipitation

This method involves the precipitation of ferric, ferrous and other ions depending on the composition of the ferrite required (see table 1.1) using an excess of alkali

$$\text{e.g. } 5NaOH + 2Fe^{+++} + Fe^{++} \rightarrow Fe_3O_4 + 5Na^{+} + 4H_2O$$

Not only does this method have the advantage that the composition can be varied by incorporating different metal ions but has two other advantages. Firstly, by the use of different alkalis the median particle size can be varied from ~4nm to >10nm and secondly the standard deviation of the particle size distribution is narrower than that produced by wet-grinding methods. Electron