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Study on the synthesis of ε-Fe_3N-based magnetic fluid

Wei Huang, Jianmin Wu*, Wei Guo, Rong Li, Liya Cui

Department of Functional Material Research, Central Iron & Steel Research Institute, Beijing 100081, PR China

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Abstract

In this work, stable high-saturation magnetization ε-Fe_3N magnetic fluid was synthesized successfully by the chemical reaction of iron carbonyl ($Fe(CO)_5$) and ammonia gas (NH_3). The experiment results have shown that the reactive conditions, such as the nitriding temperature, the gas flux ratio of Ar1:Ar2:NH_3, the reactive time, the content of surfactant and the hole size of the porous plate used, have important effects on the phase composition, the size of magnetic particles, the magnetic properties and the stability of ε-Fe_3N magnetic fluid. Also it was found that the synthetic time of stable high saturation magnetization ε-Fe_3N magnetic fluid could be shortened by adding n-heptane into the carrier, and the size of ε-Fe_3N magnetic particles could be decreased by decreasing the pore size of the porous plate used in our experiment. Finally, stable ε-Fe_3N magnetic fluid with the saturation magnetization 1663 Gs and the mean particle size 12 nm was synthesized successfully.

Keywords: Magnetic fluids; Iron nitride; Saturation magnetization; Nano-material; Functional material

1. Introduction

Magnetic fluids are stable colloidal suspension composed of single-domain magnetic nanoparticles dispersed in appropriate solvents [1] and this liquid material has an interesting superparamagnetic behaviour. The research on magnetic fluids began from 1950s. Several years later, in 1965, the magnetic fluids were used successfully for seal by the NASA, USA. After that, they became new important functional materials and were widely used for many areas, such as mechanism, electron, chemist, medical treatment, environment protection and so on.

Early in 1990s, an iron-nitride magnetic fluid was successfully synthesized by Nakatani et al. [2] using vapour–liquid chemical reaction of iron carbonyl and ammonia gas. The prominent advantage of iron-nitride magnetic fluids is its higher saturation magnetization than that of the conventional Fe_3O_4 magnetic fluids, so it was studied extensively [3–5]. In this work, the effects of the nitriding temperature, the gas flux ratio of Ar1:Ar2:NH_3, the reactive time, the content of surfactant and the hole size of the porous plate used on the phase composition and the size of magnetic particles, the magnetic properties and the stability of magnetic fluid were studied.

2. Experimental procedures

ε-Fe_3N based magnetic fluid was synthesized by a home-made apparatus (see Fig. 1). In the experiment, at first the liquid iron carbonyl ($Fe(CO)_5$) was heated to 37 °C via a water bath, the liquid iron carbonyl evaporated into the iron carbonyl vapour at this temperature. Then the iron carbonyl vapour was loaded into the bottom of the reactor (7) by argon gas (come from pipe Ar1 in Fig. 1). In the bottom of the reactor (7) the iron carbonyl vapour mixed with ammonia gas (come from pipe NH_3) and argon gas (come from pipe Ar2). The argon gas Ar2 was used to control the concentration of iron carbonyl vapour and ammonia gas in the mixed gas. And then the mixed gas went through the porous plate (5) in the middle of the reactor (7) into the carrier liquid (6) composed of α-olefinic hydrocarbon synthetic oil (PAO oil with low volatility and

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*Corresponding author. Tel.:/fax: +86 10 62183115.
E-mail address: jm1962@vip.sina.com (J. Wu).

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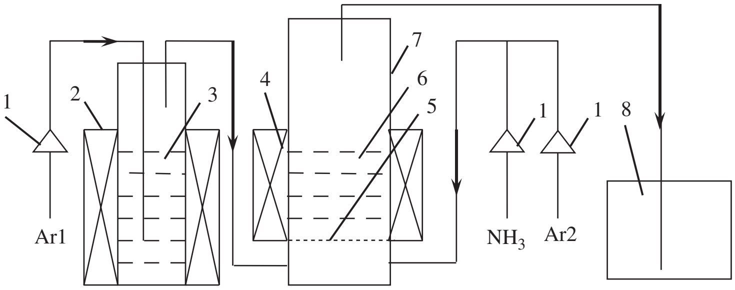

1. Flowmeter, 2. Water Bath, 3. $Fe(CO)_5$, 4. Furnace, 5. Porous Plate, 6. Carrier Liquid, 7. Reactor, 8. Exhaust Gas Bottle

Fig. 1. Preparation apparatus of the iron nitride magnetic fluid.

low viscosity) and succinicimide (surfactant). The porous plate (5) is a kind of 3 mm thickness stainless steel plate prepared by model pressing and sintering the stainless steel powders. The gas molecule could pass through this stainless steel plate from one side to the other side easily due to the existence of many fine pores inside of it. But the carrier liquid above the porous plate found it difficult to pass through it into the bottom of the reactor (7) due to the existence of the higher pressure of the mixed gas in this area. The pore size could be controlled by the prepare process. The temperature of the carrier liquid was controlled strictly at 182 °C. At this temperature, the $Fe(CO)_5$ would decompose into active ultra-fine Fe crystals. These ultra-fine Fe particles could decrease the decomposing activation energy of NH_3 from 377 to 167 kJ/mol [6] and promoted the NH_3 decomposing into N and H. The active N atoms decomposed from NH_3 diffused into Fe particles and formed iron-nitride particles. Then these iron-nitride particles were coated automatically by the surfactant and dispersed homogeneously in the carrier liquid by the Brownian motion. The iron-nitride-based magnetic fluid was obtained during this process. The volatilization velocity of the mixed oil would increase if adding some low-boiling point n-heptane into the carrier liquid in the experiment. More carrier liquid would volatilize during the same reactive time. Thus the concentration of magnetic particles increased and the magnetic fluid with higher saturation magnetization could be obtained in the same reactive time.

After synthesised, X'Pert PRO (Panalytical) X-ray diffractometer was used to analyse the phase composition of magnetic particles. The diffraction was performed with $Co_{k\alpha_1}$ ($\lambda = 1.7889$ Å) and the ray was filtered by the graphite. The experiment parameters used were: 40 mA, 35 kV, continuous scan, scan speed 2°/min. Transmission electron micrographs were obtained using a 2000fx transmission electron microscope (TEM) operated at 160 keV. Samples were prepared by air-drying drops of diluted solutions of the preparations on carbon films supported by copper grids. LDJ9600 vibrating sample magnetometer was carried out to measure the magnetic properties of magnetic fluids at room temperature. And the density was measured by the picnometer.

3. Results and discussion

3.1. Thermal decomposition temperature

The ε-Fe_3N magnetic fluids is synthesized by the reaction of $Fe(CO)_5$ and NH_3 as mentioned above. $Fe(CO)_5$ is a kind of light yellow liquid. Its boiling point is 103 °C. It decomposes into Fe and CO when heated to more than 60 °C under environmental pressure, and the decomposing speed increases with increasing temperature. In our experiment it was found that the synthetic temperature has much more effect on obtaining ε-Fe_3N magnetic fluid. The best synthetic temperature of ε-Fe_3N magnetic fluid is 182 °C. When the temperature is higher than this temperature, the size of Fe particles will grow quickly and the nano-size iron-nitride particles cannot be obtained. In addition, the stability of the mixed oil decreases. When the temperature is lower than this temperature, it is difficult to obtain the single-phase ε-Fe_3N magnetic fluid. It can be noticed that this synthetic temperature is much lower than the nitriding temperature of Fe (500–570 °C). It is because the decomposing activation energy of NH_3 is decreased by the active nascent Fe particles as mentioned above. Furthermore, the crystalline field and the binding energy of the outer layer of nano-particles are different from that of the inner layer [7]. The existence of a lot of dangling bonds around the outer layer of nano-particles makes themselves easy to combine with other atoms and form stable compounds at lower temperature.

Beside the synthetic temperature, the flux ratio of $Ar1:Ar2:NH_3$ (which decides the contents of NH_3 and $Fe(CO)_5$ in the mix gas) is also very important to the formation of single phase ε-Fe_3N magnetic fluid. It will be discussed in the next section. Fig. 2c gives the X-ray diffraction pattern of the magnetic particles synthesized at 182 °C under a proper flux ratio of $Ar1:Ar2:NH_3 = 7:2:2$. It shows that single phase ε-Fe_3N magnetic particles can be

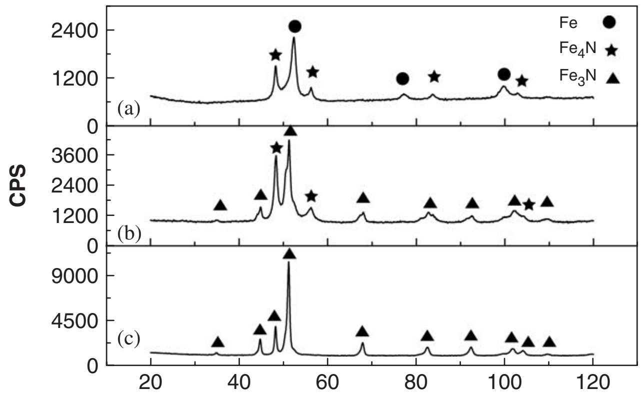

Fig. 2. X-ray diffraction patterns of the magnetic particles prepared under different Ar2: NH_3 flux rates ((a) Ar2:NH_3 = 1:0.25; (b) Ar2:NH_3 = 1:0.6; (c) Ar2:NH_3 = 1:1;).

obtained successfully at 182 °C by controlling the gas flux ratio of Ar1:Ar 2:NH_3 suitably.

3.2. The influence of gas-flux ratio

In this experiment, the relationships between the gas flux ratios of Ar1:Ar2:NH_3 and the phase compositions of the magnetic particles are studied. In order to analyse easily, the gas fluxes of Ar1 and Ar2 were fixed at 280 and 80 ml/min, respectively, and the gas flux of NH_3 was the only variable during the experiment. Thus the ratio of Ar1:Ar2:NH_3 could be expressed simply by the ratio of Ar2:NH_3.

Fig. 2 gives the relationships between the flux ratios of Ar2:NH_3 and the reactive products. The results show that when Ar2:NH_3 = 1:0.25, the reactive product was composed of Fe and Fe_4N phase (Fig. 2a). It meant that the nitriding was incomplete. The reactive product was composed of Fe_4N and Fe_3N (Fig. 2b) when the flux ratio of Ar2:NH_3 = 1:0.6. The single-phase ε-Fe_3N was obtained when the flux ratio of Ar2: NH_3 = 1: 1 (Fig. 2c). The reactive process can be expressed by the Eqs. (1) and (2):

$$\mathrm{Fe(CO)_5} \rightarrow \mathrm{Fe} + 5\mathrm{CO}\uparrow, \tag{1}$$

$$\mathrm{Fe} + \mathrm{NH_3} \rightarrow \mathrm{Fe}\langle \mathrm{NH_3}\rangle \rightarrow [\mathrm{N}]_{\text{diffuse into Fe}} + \tfrac{3}{2}\,\mathrm{H_2}\uparrow . \tag{2}$$

From Eq. (2) it can be noticed that the equilibrium constant K_P is controlled by the pressures of the NH_3 and H_2. The K_P under the different fluxes of NH_3 can be expressed by the equation

$$K_P = \frac{[P_{H_2}]^{3/2}}{P_{NH_3}}\alpha_N. \tag{3}$$

Thus

$$\alpha_N = K_P\,\frac{P_{NH_3}}{[P_{H_2}]^{3/2}}, \tag{4}$$

where K_P is the equilibrium constant of reaction (2). P_{H_2} and P_{NH_3} are the partial pressures of H_2 and NH_3 in carrier, respectively. α_N is the degree of activity of atom N in Fe particle.

Since K_P is a function of temperature, $r = P_{NH_3}/[P_{H_2}]^{3/2}$ can be regarded as the ability of nitriding at different temperatures. The experimental results show that the N content of magnetic particles increase with increasing NH_3 flux.

The non-magnetic Fe_2N phase was found when the ratio of Ar2:NH_3 decreased to less than 0.5. The existence of non-magnetic Fe_2N phase decreased the saturation magnetization of magnetic fluid. Thus, the proper flux ratio of Ar2:NH_3 is very important.

3.3. The effect of surfactant content on the stability of magnetic fluids

The magnetic particles are easy to agglomerate and settle due to their magnetic dipole interaction. When the surfactant with long chained molecules is added into the carrier liquid to coat the magnetic particles, the agglomeration and settling of magnetic particles can be avoided due to the repulsion between the magnetic particles coated by the surfactant. Of course, the surfactant must be compatible with the carrier liquid and can coat on the surface of magnetic particles. Thus, the choice of proper surfactant was very important. A kind of non-ionic surfactant (succinicimide), which is compatible very well with the carrier liquid (α-olefinic hydrocarbon synthetic oil), was found after many experiments.

The surfactant content is also very important to the stability of magnetic fluids. In order to determine the best surfactant content, different amounts of surfactant (succinicimide) were added into the carrier liquid, respectively, as shown in Table 1. And then these magnetic fluids were synthesized under the same experimental condition. After synthesized, each of the five magnetic fluids (sample FN001–005) was divided into two groups. One group was laid in the natural state and the other group was laid on the magnet.

It can be noticed from Table 1 that the settling was found for the samples FN001–003. The agglomeration and settling of particles came from the coat incompletely of surfactant due to the deficiency of surfactant content. For the samples FN004 and FN005, in which the volume ratios of surfactant were 20 and 23.8%, respectively, no agglomeration and settling were found and the stable magnetic fluid was obtained even laid on the magnet. It shows that the magnetic particles were coated completely by the surfactant and dispersed in the carrier liquid homogeneously (Fig. 3) when the volume ratio of surfactant was in the range of 20–23.8%. However, the viscosity of magnetic fluid increased with increasing the content of non-ionic surfactant (succinicimide). Thus, it was thought that the optimal content of non-ionic surfactant (succinicimide) is 20% (volume ratio).

Table 1
Effect of the contents of surfactant on the stability of the magnetic fluid

No.	Carrier (polyalphaolefin) (ml)	Surfactant (succinamide) (ml)	Laid in natural state	Laid on the magnet
FN001	80	5	Settling after 1 day	Settling immediately
FN002	80	10	Settling after 3 day	Settling gradually
FN003	80	15	Settling after 9 day	Settling slowly
FN004	80	20	No setting after 180 days	No setting after 180 days
FN005	80	25	No setting after 180 days	No setting after 180 days

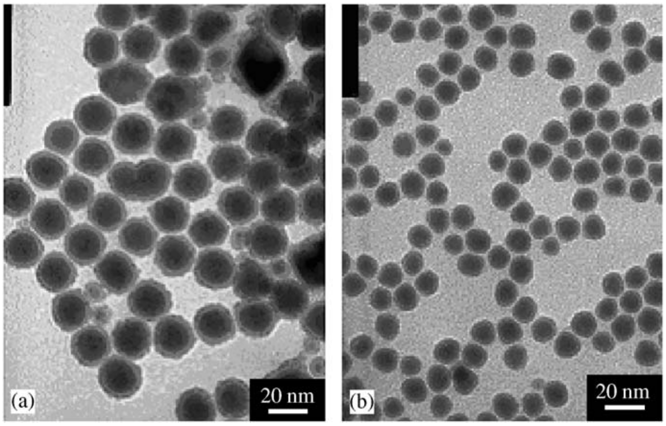

Fig. 3. TEM images of magnetic particles prepared using different porous plates ((a) the pore size range of the porous plate is 20–30 μm and the volume ratio of surfactant is 20%; (b) the pore size range of the porous plate is 5–10 μm and the volume ratio of surfactant is 20%). Both of them show that the magnetic particles were coated completely by the surfactant and dispersed in the carrier liquid homogeneously.

3.4. The effect of the porous plate on the size of magnetic particles

It has known that the size of magnetic particles has much more effects on the magnetic properties and stability of the magnetic fluids. The size of a ferromagnetic particle should be about 10^{-8} m. There are two reasons why the particles should be small. Firstly, this size provides a mono-domain structure of particles. Secondly, such particles can be suspended in the fluid by Brownian motion. Thus, it is very important to control the size of magnetic particles. The size of magnetic particles can be effected by many different factors during the synthesis of magnetic fluid, such as the reactive temperature, the surfactant content, the evaporation temperature of $Fe(CO)_5$, the gas current ratio and so on.

When all the experimental conditions mentioned above were fixed, it was found that the pore size of the porous plate used in our experiment has much more effect on the size of the magnetic particles. It has been mentioned above that the porous plate is a kind of 3 mm thickness stainless steel plate prepared by model-press and sintered the stainless steel powder. The gas molecule can pass through this stainless steel plate easily from one side to the other side due to the existence of many fine pores. The pore size can be changed by changing the density of the stainless steel plate.

Fig. 3 is the TEM images of magnetic particles synthesized using two different porous plates. It can be noticed that the size of magnetic particles shown in Fig. 3(b) is smaller than that of Fig. 3(a). It is because that the pore size of porous plates used in Fig. 3(b) is smaller than that of used in Fig. 3 (a). Also it can be found from Fig. 3 that the ε-Fe_3N particles synthesized in our experiment are sphericity and have very narrow size distributions.

According to Ref. [8], the particle size distributions can be obtained by measuring the largest dimension of each of the particle images within a defined region of a micrograph [8]. By this method, the size distributions of the magnetic particles synthesized using different porous plates were measured and are given in Fig. 4. The results show that all the fluids examined had distributions that appear approximately to be Gaussian. The mean particle sizes and the size distributive ranges of magnetic particles are given in Table 2.

It can be noticed from Fig. 4 that the size distribution of the magnetic particles increases with increasing the pore size of porous plate. It is because that the amount of vapor $Fe(CO)_5$, which passes through the porous plate in unit time, increases with increasing the pore size, namely, the content of Fe crystals in the carrier liquid increases. Thus the collision probability of Fe crystals increases and larger magnetic particles form. Therefore reducing the pore size of porous plate is an effective way to obtain the ε-Fe_3N magnetic fluid with small size magnetic particles.

3.5. Effect of the reactive time on the magnetic property

Besides the magnetic properties of magnetic particles, the content of magnetic particles (the volume fraction of magnetic particles in the magnetic fluid) has an important effect on the saturation magnetization (M_s) of magnetic fluid [8]. In order to obtain high saturation magnetization ε-Fe_3N magnetic fluid, two kinds of the methods were used to increase the volume fraction of magnetic particles. One was prolonging the reactive time; the other was adding some n-heptane into the carrier liquid before reaction.

Fig. 5 shows the magnetization curves of six samples (A–F) with different reactive times and the carrier liquids

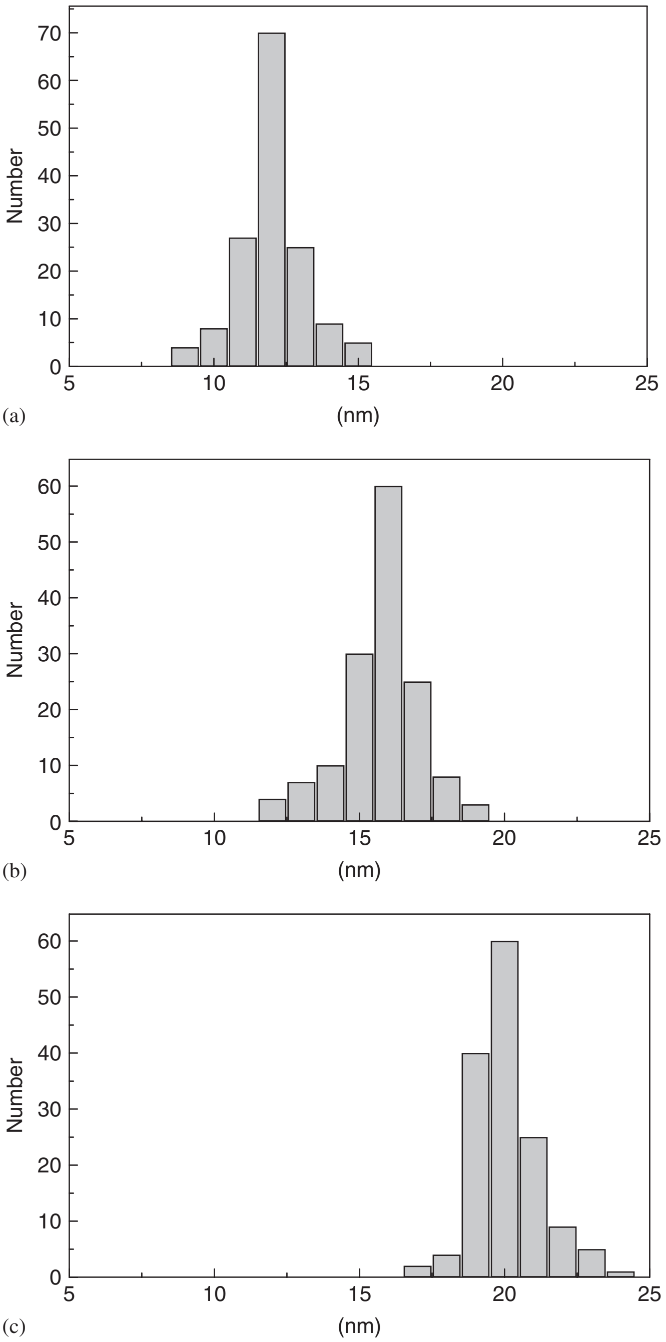

Fig. 4. Particle size distributions measured from TEM images. The pore size ranges of the porous plates used are: (a) 5–10; (b) 10–20; (c) 20–30 μm.

of samples A, E and F are composed of 80 ml α-olefinic hydrocarbon synthetic oil and 20 ml succinicimide (non-ionic surfactant). And the carrier liquids of samples B, C and D are composed of 80 ml α-olefinic hydrocarbon synthetic oil, 20 ml succinicimide (non-ionic surfactant) and 40 ml n-heptane. Fig. 6 gives the relationships between the saturation magnetizations of iron nitride magnetic fluids and the reactive times. The volume fractions of magnetic particles and the saturation magnetizations of samples A–F are given in Table 3. It can be found that the volume fraction of magnetic particles and the saturation

Table 2
Mean particle sizes and the size distributive ranges of the magnetic particles synthesized using the porous plates with different pore sizes

Pore size of the porous plate (μm)	5–10	10–20	20–30
Mean particle size (nm)	12	16	20
Size distributive range (nm)	9–15	12–19	17–24

The mean particle sizes were calculated by measured the size distributions of the magnetic particles within a defined region of TEM image.

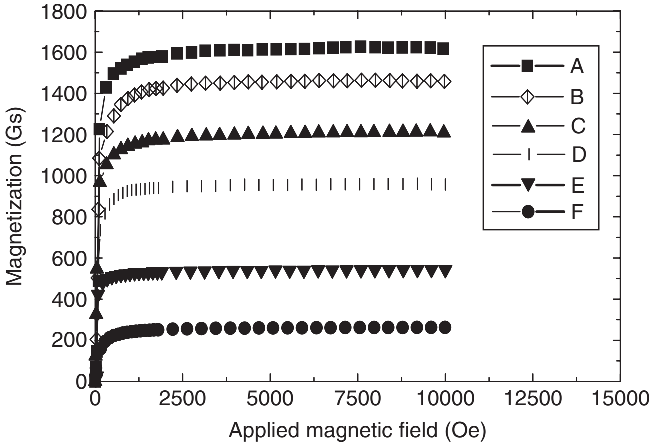

Fig. 5. Magnetization curves of the magnetic fluids prepared under different reactive times (The carrier liquid of the samples A, E and F is composed of 80 ml α-olefinic hydrocarbon synthetic oil and 20 ml succinicimide and the carrier liquid of the samples B, C and D is composed of 80 ml α-olefinic hydrocarbon synthetic oil, 20 ml succinicimide and 40 ml n-heptane. The synthetic temperature is 182 °C. The gas fluxes of Ar1 (Argon gas), Ar2 (Argon gas) and NH_3 were controlled at 280, 80 and 80 ml/min, respectively. The reactive times are B:36, C:34, D:31, A:60, E:34, F:24 h).

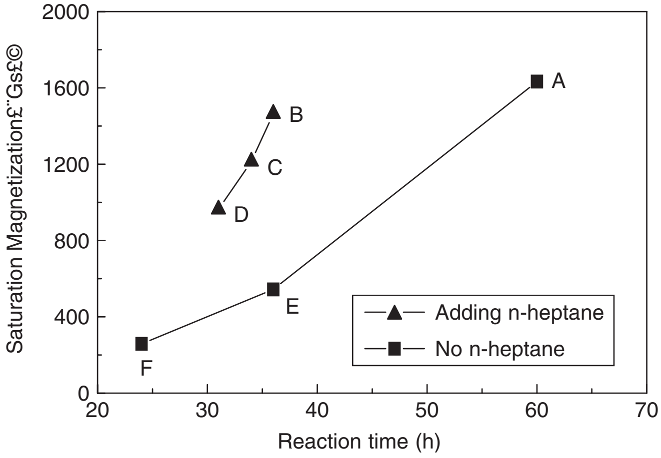

Fig. 6. Relationships between the saturation magnetizations of iron nitride magnetic fluids and the reactive times (The carrier liquid of the samples A, E and F is composed of 80 ml α-olefinic hydrocarbon synthetic oil and 20 ml succinicimide and the carrier liquid of the samples B, C and D is composed of 80 ml α-olefinic hydrocarbon synthetic oil, 20 ml succinicimide and 40 ml n-heptane. The synthetic temperature is 182 °C. The gas fluxes of Ar1 (Argon gas), Ar2 (Argon gas) and NH_3 were controlled at 280, 80 and 80 ml/min, respectively. The reactive times are B:36h, C:34h, D:31h, A:60h, E:34h, F:24h).

Table 3
The volume fractions of the magnetic particles and the saturation magnetizations of samples A–F (The carrier liquid of the samples A, E and F is composed of 80 ml α-olefinic hydrocarbon synthetic oil and 20 ml succinicimide and the carrier liquid of the samples B, C and D is composed of 80 ml α-olefinic hydrocarbon synthetic oil, 20 ml succinicimide and 40 ml n-heptane

Sample	F	E	D	C	B	A
Vol. % of the magnetic particle	1.67	3.43	6.81	8.03	10.49	10.92
Ms (Gs)	285	544	963	1214	1465	1633

The synthetic temperature is 182 °C. The gas fluxes of Ar1 (Argon gas), Ar2 (Argon gas) and NH_3 were controlled at 280, 80 and 80 ml/min, respectively. The reactive times are B: 36, C: 34, D: 31, A: 60, E: 34, F: 24 h.

magnetization of magnetic liquid increase with increasing reactive time. It also can be noticed from Figs. 5 and 6 that the magnetic fluid with higher saturation magnetization could be obtained in shorter reactive time if some n-heptane is added into the carrier liquid before reaction. The reason is that the n-heptane is a kind of low boil oil (boiling point 97 °C). The high synthetic temperature (182 °C) of ε-Fe_3N magnetic fluids will result in the evaporation of n-heptane. Since three organic solutions (α-olefinic hydrocarbon synthetic oil, succinicimide and n-heptane) have mixed together to form the homogeneous liquid, it is inevitable that the evaporation of n-heptane results in some loss of carrier and surfactant. Thus the volume fraction of magnetic particles increases during the same reactive time, and the saturation magnetization of magnetic liquid increase as shown in Table 3.

3.6. Relationship between the saturation magnetization and the density

Because the density of iron-nitride magnetic liquid is directly proportional to the volume fraction of magnetic particles, the relationships between the saturation magnetizations and the volume fractions of magnetic particles can also be expressed by the relationships between the saturation magnetizations and the densities of iron-nitride magnetic fluids as shown in Fig 7. It can be noticed that the saturation magnetization increases linearly with increase in the density of iron-nitride magnetic liquid. The relationships between the saturation magnetizations and the densities of iron-nitride magnetic liquids can be expressed by the equation

$$M_s(\rho) = -0.2025 + 0.2146\rho, \tag{5}$$

where M_s (T) is the saturation magnetization and ρ (g/cm^3) is the density of magnetic fluid. According to the Eq. (5), when $M_s = 0$, $\rho = 0.943\,\text{g/cm}^3$, which equals approximately the density of carrier liquid (0.95 g/cm^3).

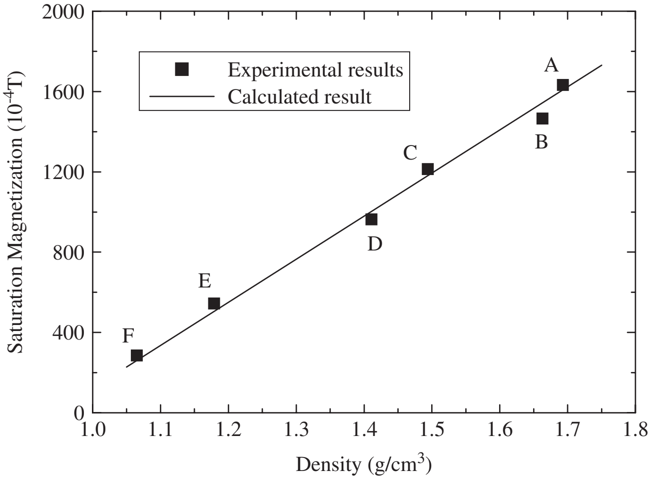

Fig. 7. Relationships between the saturation magnetizations and the densities of the magnetic liquids (■ experimental results; ▬ calculated result according to the equation $M_s(\rho) = -0.2025 + 0.2146\rho$).

4. Conclusion

ε-Fe_3N based magnetic fluid was synthesized by a home-made apparatus. The effects of the carrier compositions and the experimental conditions on the phase composition, the size of magnetic particles, the magnetic properties and the stability of ε-Fe_3N magnetic fluid were studied.

It was found that when the heat decomposition temperature of $Fe(CO)_5$ and the synthetic temperature of iron nitride magnetic fluid were controlled at 182 °C, the gas fluxes of Argon gas (Ar1 and Ar2) were controlled at 280 and 80 ml/min, respectively, the gas flux ratio of Argon gas (Ar2) and NH_3 gas was controlled at Ar2:NH_3 = 1 and the carrier liquid was composed of 80% α-olefinic hydrocarbon synthetic oil and 20% non-ionic surfactant (succinicimide) and stable single phase ε-Fe_3N magnetic fluid was synthesized successfully. The saturation magnetization (M_s) of ε-Fe_3N magnetic fluid increased with increasing reactive time. The size of ε-Fe_3N magnetic particles decreased with decreasing the pore size of porous plate used in experiment. The synthetic time of high saturation magnetization (M_s) ε-Fe_3N magnetic fluid could be shortened by adding some n-heptane into the carrier liquid before reaction. The relationships between the saturation magnetizations and the densities of ε-Fe_3N magnetic fluids could be expressed by a linear equation.

Finally, stable ε-Fe_3N magnetic fluid with the saturation magnetization 1663 Gs and the mean particle size 12 nm was synthesized successfully.

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