ELSEVIER

Journal of Alloys and Compounds 443 (2007) 195–198

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Study on the magnetic stability of iron-nitride magnetic fluid

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

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

Received 16 March 2007; accepted 6 May 2007
Available online 10 May 2007

Abstract

The effects of the addition of phenolic antioxidant on the magnetic stability of α-olefinic hydrocarbon synthetic oil based iron-nitride magnetic fluid were studied. It was found that the magnetic stability of α-olefinic hydrocarbon synthetic oil based iron-nitride magnetic fluid, both at room temperature and high temperature (80 °C), could be improved effectively by the addition of phenolic antioxidant. Only 21% magnetic decrease was found for the magnetic fluid with 5 wt.% phenolic antioxidant after exposed to atmosphere environment at room temperature for 12 months.

Thus the addition of phenolic antioxidant into α-olefinic hydrocarbon synthetic oil based iron-nitride magnetic fluid is an effective way to improve its magnetic stability.

Keywords: Iron-nitride; Magnetic fluids; Antioxidant; Nano-material

1. Introduction

Magnetic fluid (MF) is a colloidal suspension of single domain ferromagnetic particles dispersed in a liquid carrier and stabilized by means of a suitable organic surfactant [1]. It has been widely used for many areas, such as magnetic fluid seals, stereo speakers, lubricants and bearings [2]. It is well known that most magnetic fluids are made of magnetic-iron oxide (Fe_3O_4 or γ-Fe_2O_3) particles, which have much lower saturation magnetization (<70 emu g^{-1}) in comparison with Fe metal particles. In order to improve the magnetic properties of the magnetic fluid, many efforts have been devoted to making magnetic fluid with high magnetization [3–5].

Accord to Nakatani and et al. [3], the iron-nitrogen alloy system exhibits metallic phases of interstitial compounds, γ'-Fe_4N, ε-Fe_xN ($3>x>2$) and ζ-Fe_2N phase. The compound γ'-Fe_4N is ferromagnetic below 761 K with the magnetization of 186 emu g^{-1} at room temperature. The phase ε-Fe_xN is also ferromagnetic. At the composition of almost $x=3$, the Curie temperature is 567 K, and the room-temperature magnetization is 160 emu g^{-1}. Such compounds in the Fe-N system are much more resistant to oxidation than iron, and have much higher magnetizations than that of iron-oxide, Fe_3O_4. Thus, fine particles of ferromagnetic iron-nitrides have a potential application to magnetic fluids that need a high magnetization and stability against oxidation.

However, it was reported by Lee et al. [6] that the saturation magnetization of iron-nitride magnetic fluid reduces with increasing time and approaches to zero after 1008 h when exposed to the atmosphere environment. The oxidation form of iron-nitride at room temperature was considered to be non-magnetic hematite rather than magnetite and/or maghemite, which made the particles lost their magnetic properties. It shows that the iron-nitride particles do not exhibit their intrinsic excellent chemical stability. In order to stabilize nanoparticles from oxidation, a stable protective layer such as titanium, silica, aluminium was introduced on the particle surface [5–7]. The iron-nitride particles covered with titanium had a negligible effect on delaying the decrease of its saturation magnetization [6]. The stability of the magnetic fluids containing cobalt particles stabilized with $Al(C_8H_{17})_3$ and suitable surfactants can be improved remarkably [7].

In this work, the effect of the addition of phenolic antioxidant on the magnetic stability of iron-nitride magnetic fluids at high temperature and room temperature under atmospheric conditions was investigated. The results shown that the magnetic stability of iron-nitride magnetic fluid could be improved obviously by the addition of phenolic antioxidant.

---

[*] Corresponding author. Tel.: +86 10 62183115; fax: +86 10 62183115.
E-mail address: 5543837@sina.com (W. Huang).

0925-8388/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2007.05.014

2. Experimental procedure

ε-Fe_3N based magnetic fluid was synthesized according to the method reported in Ref. [8]. The carrier liquid was composed of α-olefinic hydrocarbon synthetic oil (PAO oil with low volatility and low viscosity) and succinicimide (surfactant). 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. The magnetic fluid was divided into two parts: sample A (60 ml) and sample B (15 ml). Then sample A was evenly divided into four parts of about 15 ml (A1–A4). Different amounts of phenolic antioxidant (2.5%, 5.0%, 7.5% in wt.%) were added into the A2–A4 samples, respectively. These samples were ultrasonic agitated about 1 h to ensure the homodisperse of phenolic antioxidant. LDJ9500 vibrating sample magnetometer (VSM) was carried out to measure the magnetic properties of magnetic fluid at room temperature. The magnetic field supplied by VSM is 1 T. It can be noticed from Fig. 3 that the magnetization of magnetic fluid has a very little change when the magnetic field is higher than 0.5 T. So the magnetization measured under 1 T can be considered as the saturation magnetization (M_s) of magnetic fluid. After magnetic measurement the samples A1–A4 were lay in 80 °C environment to study their magnetic stability at high temperature.

In the mean time, 5 wt.% of phenolic antioxidant was added into sample B and was ultrasonic agitated about 1 h. After magnetic measurement the samples B was exposed to ambient environment to study their magnetic stability at room temperature.

X'Pert PRO (Panalytical) X-ray diffractometer was used to analysis the phase composition of magnetic particles initial and after 12 months of sample B. The diffraction was performed with Co Kα_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.

3. Results and discussion

Fig. 1 is the TEM images of the iron-nitride particles. It can be known from Fig. 1 that the magnetic particles had an average size of 18 nm and shown very narrow size distributions. It can be observed from Fig. 1b that all the particles were coated well by the surfactant with a thickness of 2 nm and shown a typical core-shell structure.

Fig. 2 shows the relationships between the saturation magnetization and the heated time of iron-nitride magnetic fluids heated at 80 °C. The saturation magnetization of all the samples (A1–A4) decreased with increase heated time. However, higher saturation magnetization was found for the magnetic fluids with the addition of phenolic antioxidant and the decrease of saturation magnetization was A1 > A2 > A3 > A4 during the same heated time. It shown that the magnetic stability of iron-nitride magnetic fluids can be improved effectively by the addition of phenolic antioxidant. The decrease of saturation magnetization of magnetic fluid was thought that come from the corrosion of magnetic particles by the organic acid existed in the α-olefinic hydrocarbon synthetic oil.

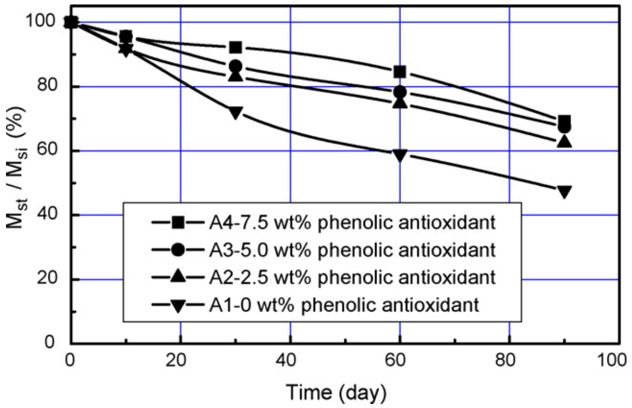

Fig. 2. Relationships between the relative saturation magnetization and the heated time of iron-nitride magnetic fluids heated at 80 °C (measured at room temperature). M_{si} is the initial saturation magnetization. M_{st} is the saturation magnetization at time t. The contents of the phenolic antioxidant for the sample A1–A4 are 0, 2.5, 5.0, and 7.5 wt.%, respectively.

According to Ref. [9], when exposed to atmosphere environment, the α-olefinic hydrocarbon synthetic oil will react with oxygen of the air according to the equation:

$$\left.\begin{array}{l} RH \rightarrow R^{\bullet} + H^{\bullet} \\ R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \end{array}\right\} \xrightarrow{\text{light or heat}} \text{organic acid} \tag{1}$$

where RH represents synthetic oil. $R^{\bullet}$ and $ROO^{\bullet}$ are two free radicals.

So it is inevitable that some organic acids will exist in α-olefinic hydrocarbon synthetic oil. It has known that this organic

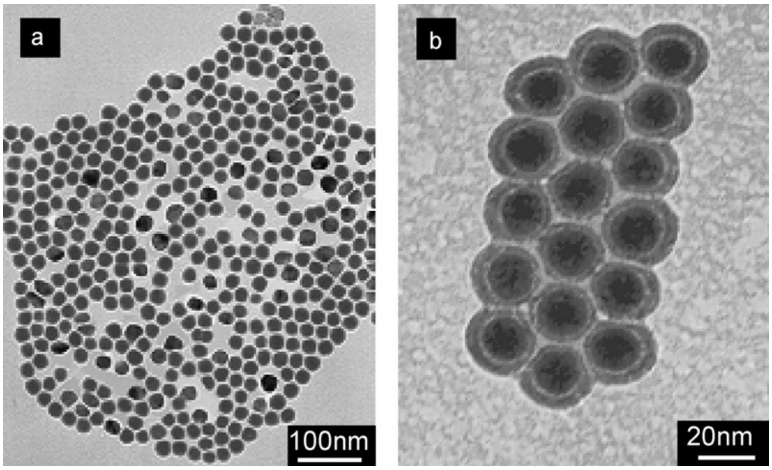

Fig. 1. The TEM images of 18 nm ε-Fe_3N particles measured immediately after the magnetic fluid prepared without any antioxidant (a: low magnified image; b: high magnified image).

acid is a kind of strong corrosive [10]. Thus the magnetic particles of magnetic fluid will be corroded by the organic acid.

Increasing temperature will conduce to the formation of organic acid and speed up corrosion of magnetic particles. Thus the saturation magnetization of magnetic fluid decreases more quickly at 80 °C than at room temperature.

When phenolic antioxidant was added into magnetic fluid, the flowing reaction happened [9]:

$$\left.\begin{array}{l}\mathrm{AH} + \mathrm{R}\cdot \rightarrow \mathrm{RH} + \mathrm{A}\cdot \\ \mathrm{AH} + \mathrm{ROO}\cdot \rightarrow \mathrm{ROOH} + \mathrm{A}\cdot\end{array}\right\} \quad (2)$$

and

$$\left.\begin{array}{l}\mathrm{A}\cdot + \mathrm{A}\cdot \rightarrow \mathrm{A{-}A} \\ \mathrm{A}\cdot + \mathrm{ROO}\cdot \rightarrow \mathrm{ROOA}\end{array}\right\} \quad (3)$$

where AH represents phenolic antioxidant.

From these reactions it can be known that the formation of some organic acid can be inhabited when phenolic antioxidant was added into the magnetic fluid, and the amount of organic acid in the magnetic fluid will decrease with increase the content of phenolic antioxidant. Thus the addition of phenolic antioxidant can decrease the oxidation and corrosion of magnetic particles and improve the magnetic stability of magnetic fluid effectively.

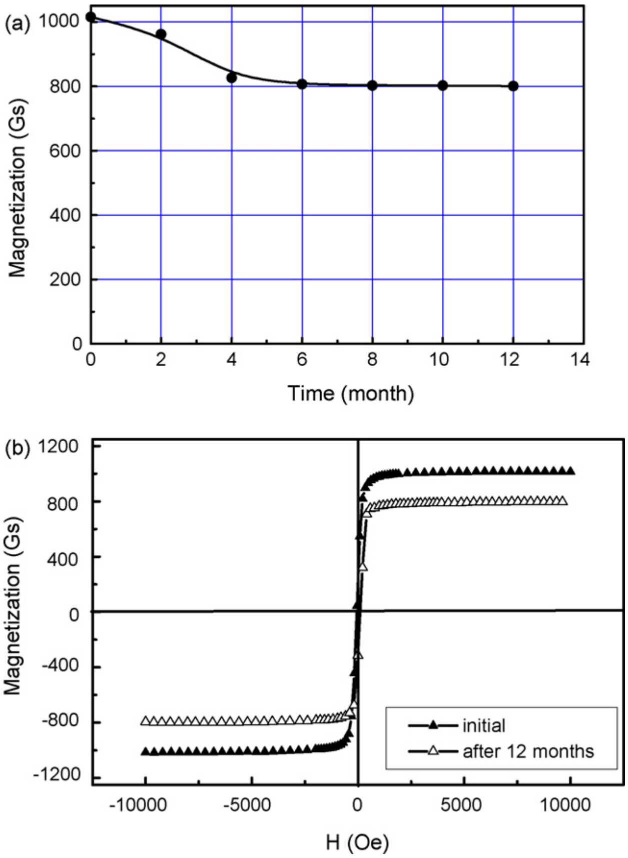

Fig. 3. (a) Relationships between the saturation magnetization and the time of sample B, which was exposed to atmosphere environment at room temperature. (b) Magnetization curves of the sample B initial and after 12 months measured at room temperature.

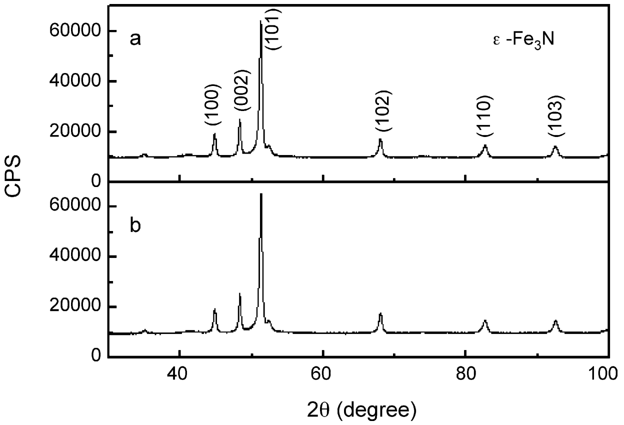

Fig. 4. X-ray diffraction results of the magnetic particles initial (a) and after 12 months (b) in sample B.

The relationship between the saturation magnetization and the time of sample B, which was exposed to atmosphere environment at room temperature, was shown in Fig. 3. It could be found that the magnetic stability of magnetic fluid was much better at room temperature than that at 80 °C for the ε-Fe_3N based magnetic fluid with the same phenolic antioxidant (5 wt.%). It was because that the decomposition speed of α-olefinic hydrocarbon synthetic oil and the formative speed of organic acid were slower at room temperature than that at 80 °C.

From Fig. 3 it could be known that the saturation magnetization of magnetic fluid decreased from 1016 to 801 Gs after 12 months. However, more quickly decrease of the saturation magnetization could be found during first four months. And then the saturation magnetization showed a very slowly decrease. Thus it was thought that some organic acid existed still in the magnetic fluid even if 5 wt.% phenolic antioxidant was added into the magnetic fluid. Accompanied with the reactions (2) and (3) mentioned above and the corrosion of organic acid on magnetic particles, the content of organic acid would decrease progressive. So the magnetic change as shown in Fig. 3 was observed.

Fig. 4 gives the X-ray diffraction results of the magnetic particles initial and after 12 months in sample B. Both of them are composed of single phase ε-Fe_3N.

4. Conclusion

The effects of the addition of phenolic antioxidant on the magnetic stability of α-olefinic hydrocarbon synthetic oil based iron-nitride magnetic fluid were investigated. It was found that the magnetic stability of α-olefinic hydrocarbon synthetic oil based iron-nitride magnetic fluid, both at room temperature and high temperature (80 °C), could be improved effectively by the addition of phenolic antioxidant. The reason is that the formation of some organic acid can be inhabited when phenolic antioxidant was added into the magnetic fluid. Thus the corrosion of magnetic particles can be decreased.

The experimental results shown that for the magnetic fluid with 5 wt.% phenolic antioxidant, its saturation magnetization decreased from 1016 to 801 Gs (only 21% decrease) after exposed to atmosphere environment at room temperature for 12 months. Thus the addition of phenolic antioxidant into α-olefinic hydrocarbon synthetic oil based iron-nitride magnetic fluid is an effective way to improve its magnetic stability.

Acknowledgement

This work was supported by the national 863 project (no. 2002AA302608), from the Ministry of Science and Technology, China.

References

[1] B.M. Berkovsky, Magnetic Fluids Engineering Applications, Oxford University Press, Oxford, 1993.
[2] L.Q. Yu, L.J. Zheng, J.X. Yang, Mater. Chem. Phys. 66 (2000) 6–9.
[3] I. Nakatani, T. Furubayashi, J. Magn. Magn. Mater. 85 (1990) 11–13.
[4] M. Wageber, B. Gunther, J. Magn. Magn. Mater. 210 (1999) 41.
[5] T. Atarashi, Y.S. Kim, T. Fujita, K. Nakatsuka, J. Magn. Magn. Mater. 201 (1999) 7–10.
[6] H.S. Lee, I. Nakatani, J. Magn. Magn. Mater. 201 (1999) 23–26.
[7] H. Bönnemann, W. Brijoux, R. Brinkmann, N. Matoussevitch, N. Waldöfner, Inorg. Chim. Acta 350 (2003) 617–624.
[8] W. Huang, J. Wu, W. Guo, R. Li, L. Cui, J. Magn. Magn. Mater. 307 (2006) 198–204.
[9] X. Tang (Ed.), Action Principle and Application of Oil Processing Agent, Petrochemical Industry Press, 2004, p. 121 (in Chinese).
[10] T. Mang, W. Dresel (Eds.), Lubricants and Lubrication, Petrochemical Industry Press, 2003, p. 74 (translated by X. Zhao and J. Wang) (in Chinese).