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Interaction of superparamagnetic and non-superparamagnetic particles in magnetic fluid

B. Jeyadevan *, K. Nakatsuka

Dept. of Resources Eng., Tohoku University, Sendai 980, Japan

Abstract

Magnetic fluids are known to contain superparamagnetic and non-superparamagnetic particles. In this paper, an attempt has been made to show the interaction between superparamagnetic and non-superparamagnetic particles experimentally by measuring the initial susceptibility, over a wide temperature range, of manganese–zinc ferrite and cobalt ferrite magnetic fluids both separate and as mixtures. Likewise experiments were done with manganese–zinc ferrite and magnetite magnetic fluids. The results showed that when the percentage of non-superparamagnetic particles is high, the interaction is high when the particle rotations are restricted. The interaction was less for the system where the non-superparamagnetic particle fraction is small, as in the case of manganese–zinc ferrite and magnetite mixture. The above was true for both zero field cooled and field cooled cases.

1. Introduction

The particles in a magnetic fluid (MF) can be either non-superparamagnetic (non-SP) or superparamagnetic (SP) depending on their anisotropy. Magnetite, Mn–Zn ferrite and cobalt ferrite MFs showed no difference in magnetic behavior in the liquid state [1,2]. Differences did show up, however, when the samples are cooled below the freezing point of the solvent (~ 220 K). In this paper we examine the effect of the interaction of permanent magnetic (non-SP) and superparamagnetic (SP) particles on the magnetic response by measuring the initial susceptibility, over a wide temperature range, of manganese–zinc ferrite and cobalt ferrite magnetic fluids, both separate and as a mixture. Likewise, experiments were done with manganese–zinc ferrite and magnetite magnetic fluids.

2. Experimental

The samples for the study were prepared by mixing kerosene based (a) cobalt ferrite MF with Mn–Zn ferrite MF and (b) Mn–Zn ferrite MF with magnetite MF each in equal volumes. Specified volume of the samples were used for individual measurements and the same samples were mixed and the volume of the mixed sample was brought to the specified volume by evaporating the solvent. The χ_i measurements on samples cooled under 0, 700 Oe are made in the temperature range 83–293 K by induction method (accuracy ± 0.002 units). The cooling field and the measuring field were in the same direction.

3. Results and discussion

The initial susceptibilities of magnetic fluids containing magnetite, Mn–Zn ferrite and cobalt ferrite particles over a wide temperature range have been carried out and the results have been reported [1,2]. In the liquid state, the above fluids showed superparamagnetic behavior. However the differences show up markedly when the rotational freedom of the particles are restricted through solidification of the medium by cooling down below the freezing point of the solvent. The χ_i–T relations of Mn–Zn ferrite, cobalt ferrite and magnetite containing fluids are given in Fig. 1. It can be seen that the above relation differs very much when the magnetite and cobalt ferrite magnetic particles loose their rotational freedom on freezing of the fluid. In the case of Mn–Zn ferrite magnetic fluid there is no obvious change in χ_i over the freezing point, so it could be said that this magnetic fluid consists of a fairly large percentage of SP particles. The peak around 110 K is believed to be the average blocking temperature (T_B) of the dispersed particles. In the case of the cobalt ferrite magnetic fluid, when the particles loose their rotational

* Corresponding author. Fax: +81-22-222 2114.

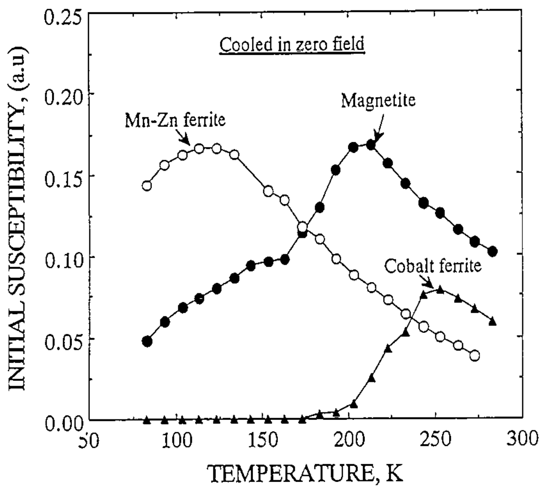

Fig. 1. The χ_i–T relation for kerosene based Mn–Zn ferrite, cobalt ferrite and magnetite magnetic fluids under zero field cooling.

freedom, they do not respond to fields less than their coercive field and the initial susceptibility becomes zero. Therefore, it could be said that this fluid consists almost only of non-SP particles. In the case of the magnetite magnetic fluid, the results suggest the presence of both SP and non-SP particles. It is interesting to know the effect of the interaction between SP and non-SP particles in a magnetic fluid. This interaction can be studied by preparing samples of mixed magnetic fluids with different proportions of non-SP particles and measuring their initial susceptibilities over a wide temperature range.

3.1. Cobalt ferrite Mn–Zn ferrite mixed MF

(a) Magnetic fluids cooled under zero field

The χ_i–T relations of mixed and the individual MFs are shown in Fig. 2. The results suggest that the cobalt ferrite particles are almost totally non-SP particles and Mn–Zn ferrite has a large percentage of SP particles having its average blocking temperatures (T_B) around 110 K. The mixed fluid of equal volumes of the individual fluids with a solid concentration of 9.0 vol% contains almost equal quantities of non-SP and SP particles. In the absence of particle–particle interaction, the χ_i of mixed MF at temperatures below the melting temperature of the solvent ($T_m = 220$ K) is expected to take values similar to Mn–Zn ferrite MF, since χ_i of cobalt ferrite MF in this temperature range is zero. In the temperature range above T_m, we expect the χ_i to be equal to the sum of the individual χ_i values of Mn–Zn ferrite and cobalt ferrite MF at the respective temperatures. The χ_i of the mixed fluid at temperatures less than T_m is found to be less than that of Mn–Zn MF prior to mixing. It may be argued that the increase in solid concentration, that decreases the interparticle distance and thereby gives rise to higher particle–particle interaction, may have caused the decrease in χ_i values. However, the χ_i measurements of Mn–Zn ferrite fluid having a solid concentration a little higher than the mixed fluid, showed a χ_i maximum value of about three times that of Mn–Zn ferrite magnetic fluid cooled in zero field [2]. This suggests that the presence of non-SP cobalt ferrite particles in the vicinity of the SP Mn–Zn ferrite particles below T_m, hinders the rotation of the magnetic vectors of Mn–Zn ferrite particles, thereby reducing χ_i. At temperatures higher than T_m, cobalt ferrite as well as the Mn–Zn ferrite particles have rotational freedom and particle–particle interaction above T_m gives a positive effect (χ_i of mixed is greater than the simple addition of the two values prior to mixing). The apparent shift in the peak of χ_i above T_m is believed due to the continued influence of the non-SP cobalt ferrite particles on SP Mn–Zn particles.

(b) MFs cooled in an external field

The χ_i–T relations for Mn–Zn, cobalt ferrite and mixed MF cooled in a magnetic field of 700 Oe, are given in Fig. 3. The high χ_i of the Mn–Zn ferrite MF in the solidified region is believed due to chains formed while cooling [2]. If the chain is composed predominantly of SP particles with T_B very much below T_m, the field induced texture will influence the alignment of the particle magnetic vector in a chain. In the mixed MF, the composition of the chains will be a mix of non-SP and SP particles for which T_B is greater than T_m, for the blocked particles. Thus the blocked particles will tend to keep the moments of the SP particles aligned and hinder their co-operative rotation of particle moments. In the solidified region, the χ_i for the mixed MF is much lower than the values

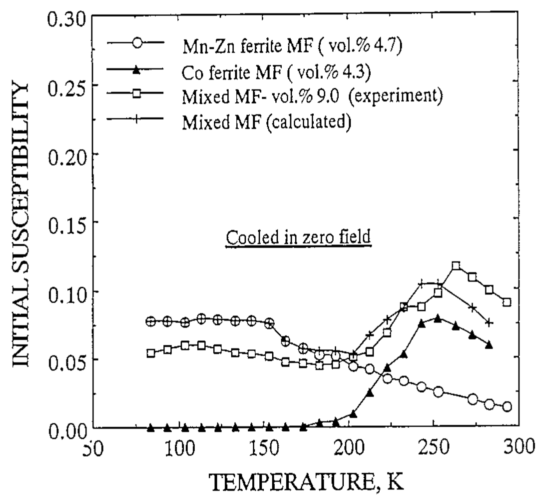

Fig. 2. The χ_i–T relation for kerosene based Mn–Zn ferrite, cobalt ferrite and mixed magnetic fluids cooled in zero field.

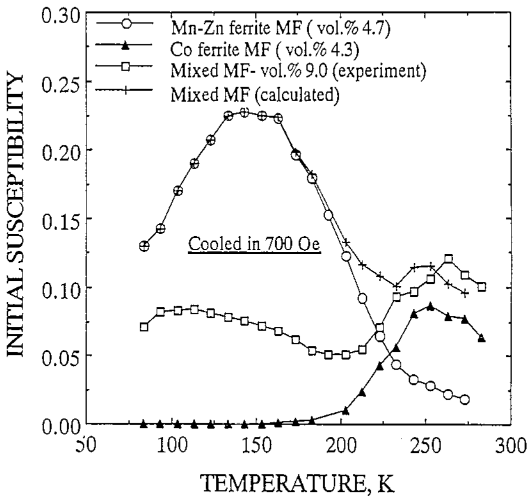

Fig. 3. The χ_i–T relation of kerosene based Mn–Zn, cobalt ferrite and mixed magnetic fluid cooled in 700 Oe.

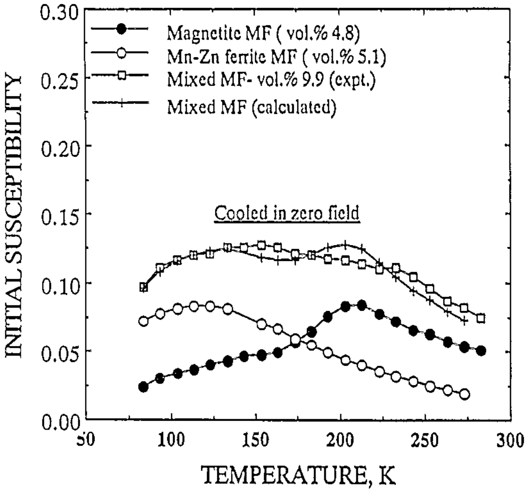

Fig. 4. The χ_i–T relation of kerosene based Mn–Zn, cobalt ferrite and mixed magnetic fluid cooled in 700 Oe.

obtained for Mn–Zn ferrite MF alone but a little higher than the zero field case. Therefore, it is reasonable to believe that the reduction of χ_i values was due to interaction among SP and non-SP particles.

3.2. *Mn–Zn ferrite–magnetite mixed MF*

(a) Magnetic fluid cooled under zero field

Unlike in the case of cobalt ferrite particles where almost all the particles in the system are non-SP in the experimental temperature range, the magnetite particles have their magnetic moment blocked at lower temperatures and a substantial percentage of the particles respond below T_m. Therefore, the effect of particle–particle interaction will be maximal in the lower temperature region. The χ_i–T curves of the Mn–Zn ferrite and magnetite MFs cooled under zero field are shown in Fig. 4. In the case of Mn–Zn ferrite, magnetite mixed MF (Fig. 4) χ_i is very much close to the sum of χ_i values of Mn–Zn and magnetite MFs measured separately. But, it should be noted that the observed χ_i of mixed fluid is slightly higher than the expected value in the temperature range of 130–180 K and lower in the range of 180–220 K. This may have been due to the shift in the average T_B of the system as a result of mixing magnetite particles with the Mn–Zn ferrite. These results suggest that in this system the hindrance of SP particles by SP particles is realized only at very low temperatures as blocking of the magnetic vector of large number of particles are realized at lower temperatures.

(b) MF cooled under an external field

The application of an external field induces chain formation in addition to the elongation of closed aggregates if there are any. Introducing magnetite into Mn–Zn ferrite magnetic fluid will increase the possibility of having non-SP particles that exert influence on the SP particles in the chain.

The χ_i–T curve for the mixed MF is given in Fig. 5; its shape is similar to that of Mn–Zn ferrite MF, except for the fact that the maximum is shifted to around 170 K. The increase in χ_i up to the maximum for increasing temperature is due to the enhancing effect caused by unblocking of the magnetic vector of Mn–Zn ferrite as well as magnetite particles. At the right side of the maximum the randomizing effect due to thermal agitation is more dominant than the enhancement due to unblocking. The shift of the maximum of mixed MF towards higher temperature is due the change in average T_B.

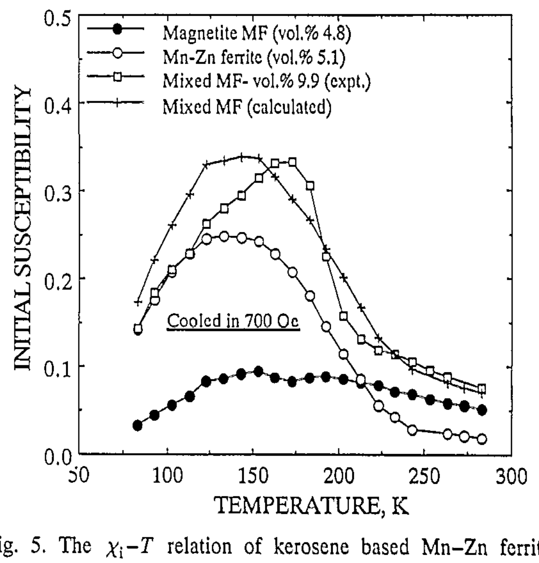

Fig. 5. The χ_i–T relation of kerosene based Mn–Zn ferrite, magnetite and mixed magnetic fluid cooled in 700 Oe.

The maximum value of χ_i for field cooled sample is about three times that of zero field cooled. This is believed due to the effect of structure induced by field cooling and the co-operative effect of particle magnetic moments that is in operation even in the mixed MF. The above results confirm that the inter-particle interaction hindering rotation of particle magnetic moment is less if the fraction of non-SP particles is small.

4. Conclusion

Due to particle interaction, the initial susceptibility of mixed magnetic fluids is modified when cooled in zero field and enhanced when the system is structured by the influence of external magnetic field. The results of cobalt/Mn–Zn mixed MF confirms that the non-SP particles do exert influence on SP particles in their vicinity and hinder the movement of the particle magnetic vector. The results of the Mn–Zn ferrite/magnetite mixed MF show that the hindrance of the movement of the particle magnetic vector through particle–particle interaction is less when the fraction of non-SP is small.

References

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[2] K. Nakatsuka and B. Jeyadevan, IEEE Trans. Magn. 30 (6) (1994) 4671.