Liquid Gallium based Temperature Sensitive Functional Fluid Dispersing Chemically Synthesized FeMB Nanoparticles

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Abstract. In this work, FeMB (M = Nb, V) nanoparticles were first reported to be synthesized by a chemical method, from reduction of FeCl$_2$, NbF$_5$ (and NH$_4$VO$_3$) using NaBH$_4$ as a reducing agent in aqueous solution. A new temperature sensitive functional fluid was then prepared by dispersing silica coated FeNbVB nanoparticles in liquid gallium. The result shows that the FeNbVB nanoparticles exhibit an oxidation resistance better than that of FeNbB nanoparticles. The FeNbVB nanoparticles were in the size range of 30 - 50 nm and the thickness of silica layer was observed about 10 nm by means of transmission electron microscopy. The magnetization of the synthesized particles and fluid shows a temperature dependency within the testing temperature range of 293 - 353 K, which indicated their application potential in magneto-caloric energy conversion devices.

1. Introduction

A functional fluid is a good choice for the application in magnetocaloric energy conversion and heat exchange devices, where a high thermomagnetic coefficient is required. However, the most widely used functional fluids, prepared by dispersing magnetite nanoparticles in water, can not satisfy these requirements [1]. Therefore, the development of temperature sensitive magnetic nanoparticles for functional fluids is of great interests. Especially, FeMB (M = Zr, Hf, V, Nb, Ti, Ta, Mo and W) nanocrystalline alloy is an excellent type of soft magnetic materials characterized by its high saturation and permeability [2, 3] that, as recently it is reported, show also magneto-caloric effect [4-7]. Nowadays, iron based alloys are mainly fabricated by metallurgical methods, such as arc-melting [8, 9] and mechanical alloying [10, 11], by which nano-sized and homogenously distributed particles are difficult to be obtained. On the other hand, chemically synthesized magnetic materials may have unique magnetic properties, derived from their small particles sizes and uniform size distribution [12, 13]. Thus, developing a chemical synthesis method to prepare temperature sensitive FeMB nanoparticles is of great interests.

On the other hand, when selecting a carrier liquid, it is important to consider the melting point, boiling temperature and evaporation at working temperature. A good carrier for temperature sensitive functional fluids can be a liquid metal, which exhibit a high thermal and electric conductivity as well as fluidity. When ultra fine particles are dispersed in a liquid metal, the functional fluid such as magnetic fluid and magneto-rheological fluid can be prepared. For many years, the synthesis of the mercury based magnetic fluid has been investigated, however, liquid mercury is toxic and difficult to handle. Thus, an environment-friendly alternate, liquid gallium becomes a good choice for the carrier liquid in functional fluid. In particular, gallium has the advantages of remaining in the liquid state throughout a wide temperature range (303 to 2477 K) and has a very low vapour pressure at atmospheric pressure (9.31×10$^{-21}$ Pa at 302.9 K). It has high thermal conductivity which is much higher than that of traditional organic or aqueous carrier liquids [14]. Thus, liquid gallium-based functional fluids can be used in magneto-caloric energy conversion devices or heat exchange devices, where continuous heat diffusion and cooling can be achieved and the elastic properties can be kept at all times [15]. The aim of this work is to prepare the...
liquid gallium based temperature sensitive functional fluid. Here, we report for the first time the synthesis of FeMB nanoparticles by a chemical method. In order to increase the affinity of the nanoparticles to liquid gallium, silica coating on FeNbVB particle surface was then carried out by the sol-gel method, based on the hydrolysis and condensation of TEOS (tetraethyl-orthosilicate). Our attentions were focused on the preparation and the temperature dependency of magnetization of the synthesized magnetic nanoparticles and functional fluid.

2. Experimental method

2.1 Preparation of FeMB nanoparticles and silica coating procedure

FeNbVB nanoparticles were prepared by a chemical synthesis based on sodium borohydride reduction. A mixed aqueous solution of niobium fluoride 97% (NbF₅, Aldrich), ammonium vanadate 99% (NH₄VO₃, Wako) and iron (II) chloride tetrahydrate 99% (FeCl₂·4H₂O, Nacalai,) was precipitated by using 336 mmol of sodium borohydride 98% (NaBH₄, Nacalai) solution. Reagents of NbF₅, FeCl₂·4H₂O and NaBH₄ were dissolved separately in distilled water. NH₄VO₃ was dissolved in water by adding of 0.5 mol/l sulfuric acid solution. NaBH₄ solution was simultaneously added into the mixture containing the Fe, Nb and V ions. The synthesized particles were then washed several times with ethanol. FeNbB nanoparticles were also prepared in the same way, only without the addition of ammonium vanadate. Finally, the synthesized particles were collected by means of filtration, and dried in a desiccator at room temperature. Details of the preparation of the silica coated magnetic nanoparticles were given in a previous publication [16]. Finally, theses core-shell nanoparticles were dispersed in the liquid gallium at the solid weight fraction of 1.67 mass%.

2.2 Composition analysis and characterization

The composition of the sample was determined with inductively coupled plasma optical emission spectrometry (Optima 5300 DV, PerkinElmer) and field emission scanning electron microscope (JSM-7000F, JEOL) equipped with EDS (energy dispersive spectroscopy). The morphology of core-shell type nanoparticles and the thickness of silica layer were observed by using a transmission electron microscope (JEM-2000FX, JEOL) equipped with EDS. Vibrating sample magnetometer (VSM) was also employed to investigate the temperature dependency for the magnetization of samples. The applied magnetic field was varied between 0 and 0.9 T.

3. Results and discussion

3.1 Morphology and composition of FeMB nanoparticles

The content of Fe, Nb, V and B in the samples was qualitatively determined by inductively coupled plasma optical emission spectrometry (ICP-OES), and the results were shown in Table 1. It can be seen that the ratio of iron, niobium and boron is about 78, 7 and 15 mol % for the FeNbB nanoparticles. A drawback is that Nb has lower resistance to oxidation at an elevated temperature. In order to overcome the oxidation problems, 4 mole % of vanadium ion was contained in this work.

Table 1. The normalized element compositions of the samples, determined from ICP-OES analysis.

|          | Fe   | Nb  | V     | B     | Total |
|----------|------|-----|-------|-------|-------|
| FeNbB    | 77.88| 7.17| -     | 14.95 | 100   |
| FeNbVB   | 80.28| 2.84| 3.75  | 13.13 | 100   |

The synthesized FeNbVB nanoparticles have a ratio of iron, niobium, vanadium and boron around 80, 3, 4 and 13 at mole %. As shown in Figure 1, the as-synthesized FeNbVB nanoparticles have a smaller particle size in general, and are not aggregated as much as FeNbB particles. The EDS data also showed that the content of oxygen of FeNbVB samples is largely reduced from 46.67 % to 15.25 %.
3.2 Morphology and composition of FeNbVB-SiO$_2$ core-shell nanoparticles

Generally speaking, naked metal powders are not dispersed easily in the liquid gallium directly; on the other hand, refractory metals and ceramics, such as tantalum, tungsten, graphite, stabilized ZrO$_2$, and quartz are most stable in gallium [17]. Therefore, in this work, FeNbVB nanoparticles were coated with silica in order to improve the dispersability of these particles in liquid gallium. Another reason for selecting silica coating, it is possible to prepare the core-shell composite particle consisting of a FeNbVB core and a silica coating layer, with a density similar to that of the liquid gallium [14].

Figure 2 depicts the TEM images and EDS data of the FeNbVB and FeNbVB-SiO$_2$ core-shell nanoparticles. The FeNbVB particles are mostly in the size range of 30 - 50 nm. By placing the electron beam exactly on these spherical particles, peaks for iron, niobium and vanadium have been observed (Figure 2(a)), and a shell of SiO$_2$ with a thickness of about 10nm was also be observed on the FeNbVB particles (Figure 2(b)). The formation of silica can be observed from the composition analysis of the coated particles. Also the density of the core-shell particles can be adjusted by controlling the thickness of silica coating layer.

The macroscopic observation of different particles mixed with liquid gallium is shown in Figure 3. The result clearly shows that the FeNbVB particles without coating can hardly be dispersed into liquid gallium, so that Figure 3(a) shows two separated phase i.e., residual FeNbVB particles and liquid gallium. A small amount of metal powders could be directly dispersed and a small amount of powders tended to remain on the surface of liquid gallium. Figure 3(b) shows that the silica coated FeNbVB particles can be well dispersed into liquid gallium, which keeps its brilliant silvery colour. Moreover, the contact angle at
the iron and SiO\textsubscript{2} substrate / liquid gallium interface was 158° and 145°, respectively. Contact angles were measured directly from the image of the drop section by using a digital microscope (Keyence VHX-100), equipped with an 18 million-pixel CCD camera. The measurement of initial contact angel between pure liquid gallium (99.9999 %, 0.1 mL) and substrate samples were conducted at 313 K under atmospheric pressure. This result also shows that silica coated FeNbVB particles can be easily wetted by liquid gallium, relatively when compared with FeNbVB particles without silica coating. Therefore, it is reasonable to conclude that the existence of silica coating improves the dispersion of FeNbVB particles into liquid gallium.

Figure 3. Macroscopic observation of FeNbVB particles mixing with liquid gallium (1.67 mass% of solid fraction, \( T = 293 \text{ K} \)) and contact angle of iron and silica for liquid gallium (\( T = 313 \text{ K} \)). (a) FeNbVB particles without coating and contact angle of iron for liquid gallium (b) silica coated FeNbVB particles and contact angle of silica for liquid gallium.

3.3 Temperature sensitive magnetic property of as-synthesized samples

Figure 4 shows that the magnetization curve for the samples measured between 293 K and 353 K in 5 K steps and the temperature dependencies of the magnetization for FeNbVB nanoparticles (Figure 4(a)), and silica coated FeNbVB (Figure 4(b)) nanoparticles measured in an applied field 0.9 T. The result shows that the temperature dependency of the magnetization for the silica-coated FeNbVB nanoparticles is almost same as the FeNbVB nanoparticles, though the magnetization values decrease due to the existence of a non-magnetic silica layer (Figure 2(b)). The result shows that the synthesized FeNbVB particles have a little lower saturation magnetization and temperature dependency than FeMB soft magnetic alloy prepared by metallurgical methods [5-7]. However it has relatively high saturation magnetization and temperature dependency when compared with various types of temperature sensitive ferrite such as Ni-Zn and Mn-Zn ferrite etc. [18-20], which are normally applied to magneto caloric energy conversion or heat exchange device. Moreover, chemically synthesized FeNbVB magnetic particles have smaller particles sizes and uniform size distribution than FeMB magnetic alloy obtained from metallurgical methods. Therefore, chemically synthesized FeNbVB magnetic particles more suitable to prepare the liquid gallium based functional fluid. On the other hand, Figure 4(c) shows that the temperature dependency of liquid gallium based functional fluid dispersed silica coated FeNbVB nanoparticles (1.67 mass% of solid fraction). The magnetization value of the synthesized functional fluid decreases, which is caused by the low magnetic property of liquid gallium and low solid fraction of magnetic particles. However, the magnetization value of the synthesized functional fluid still shows the temperature dependence, i.e. decreases with increasing temperature.

4. Conclusion

In this study, the liquid gallium based temperature sensitive functional fluid, dispersing silica coated FeMB nanoparticles was synthesized. The result shows that the FeNbVB nanoparticles exhibited an oxidation resistance higher than that of FeNbB nanoparticles. The FeNbV nanoparticles were in the size range of 30 - 50 nm and the thickness of silica layer was about 10 nm. Both the synthesized nanoparticles and functional fluid showed a temperature sensitive of magnetization within the testing temperature range of 293 - 353 K. Therefore, the liquid gallium based temperature sensitive functional fluid dispersing silica coated FeNbVB nanoparticles is considered as an attractive working liquid for magneto-caloric energy conversion and heat exchange applications due to a high saturation magnetization and a high temperature dependence even low solid fraction.
Figure 4. Magnetization curve for the samples measured between 293 K and 353 K in 5 K steps and the temperature dependencies of the magnetization for the samples measured at an applied field of 0.9 T. (a) FeNbVB, (b) FeNbVB-SiO$_2$ and (c) synthesized liquid gallium based functional fluid.

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