Magnetic properties of glass ceramic wire in Fe₃O₄-TiO₂-SiO₂ system

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Abstract. A glassy composite magnetic wire was prepared by elongation during quenching phase-separated melt in two-liquids stable immiscibility region of Fe₃O₄-TiO₂-SiO₂ ternary system. The glass-ceramics in the Fe₃O₄-TiO₂-SiO₂ system has a phase-separation texture, which consisted of Fe₃O₄-TiO₂-rich and SiO₂-rich phases, and shows ferromagnetic properties. The internal textures of wire samples were needle-like structure parallel to the direction of the elongation. The wire sample had larger saturated magnetization and lower coercive force than those of non-elongated bulk one.

1. Introduction
Magnetic materials are widely used for various electronic applications such as a permanent magnet and a magnetic sensor. Recently, preparation of hybrid magnetic material is of particular interest because of the wide range of possible applications: not only in the electronic applications but also in bio- and medical technology. For example, a hyperthermia treatment of tumors using magnetic material is known as one of the treatments for cancer [1], and a ferro-, ferri- or superparamagnetic plate, needle or particles have been investigated [2-7]. An important requirement of the materials for the biomedical application is biocompatibility.

A phase separation in a glass material is very popular phenomenon, and there are two types of phase separation texture, which are called nucleation-growth process and spinodal decomposition one. A texture of the former consists of discrete fine droplets and continuous matrix. A texture of the latter consists of three-dimensionally interconnected two phases. The conventional application of the phase-separated glass is the glass with high thermal and chemical durability and the porous glass in Na₂O-B₂O₃-SiO₂ system that are well known as Pyrex® and Vycor® glass, respectively. Recently, the phase-separated glasses have found broad application such as phosphor [8-12], photocatalytic [13, 14] and magnetic materials [15-18].

We have investigated phase-separated glass-ceramics in Fe₃O₄-TiO₂-SiO₂ system prepared by a melt-quenching method, and the obtained glass-ceramics showed ferromagnetic and electrical conductive properties [17]. The phase-separated textures can be deformed into needle-like shape by elongation during quenching the melt in the system of Fe₃O₄-SiO₂ [15] and CaO-Fe₃O₄-SiO₂ [16], and act as anisotropic functional composite materials [16]. In this study, the melts in the Fe₃O₄-TiO₂-SiO₂
system were quenched with elongation, and the morphology of internal texture, precipitated crystalline phase and magnetic property of the elongated wire and the non-elongated bulk sample were examined.

2. Experiments

The compositions of two-liquids immiscible melt were $x\text{Fe}_2\text{O}_4\gamma\text{TiO}_2(100-x\gamma)\text{SiO}_2+5\text{Al}_2\text{O}_3$ (mol%, $x=15.0, 22.5, 30.0, y=x/3$). The small addition of alumina improves the compositional homogeneity of glass melt, and makes the phase separation texture finer in the obtained glass. Starting raw materials of $\text{Fe}_2\text{O}_3$, $\text{TiO}_2$, $\text{SiO}_2$ and $\text{Al}_2\text{O}_3$ were mixed by ball-milling for 24 hour in ethanol. After drying, the obtained batches were molded into a rod shape by use of a cold isostatic press. The rods were sintered at 1200 °C for 12 h in air. The sintered rod samples were melted for 3 min by use of an infrared imaging furnace (ULBAC, PRC MR-H500) and quenched by turning off the halogen lamps of the furnace. In the preparation method of a wire sample, the tip of the sintered rod was melted in the furnace for 3 min and the melting droplet was contacted with an alumina rod, and then immediately pulled up at 10mm/sec.

The crystalline phases of the quenched samples were analyzed by a powder X-ray diffraction (XRD, SHIMADZU, XRD-6100). Magnetic properties of the samples were evaluated from their magnetization curves, which were obtained by use of a vibrating sample magnetometer (VSM, Riken Denshi Model BHV-55). The melt-quenched samples were cut vertically and polished, and their phase-separation textures were observed by a scanning electron microscope (SEM, JEOL, JSM-5800LV).

3. Results and discussion

3.1. Crystalline phase

The XRD patterns of bulk and wire samples are shown in Figure 1. The sharp diffraction peaks of bulk samples were identified as spinel phase of $\text{Fe}_2\text{O}_4$ or $\text{Fe}_2\text{O}_3\gamma\text{TiO}_2$ solid solution. An amorphous halo due to $\text{SiO}_2$-rich phase was slightly observed at around 22° in all the samples. In the bulk sample of $x = 30.0$, the weak diffraction peaks of hematite ($\alpha\text{-Fe}_2\text{O}_3$) phase were also observed. The precipitation of $\alpha\text{-Fe}_2\text{O}_3$ phase is principally due to oxidation of iron (II) to iron (III). The reason for the oxidation of iron ion in the sample of $x = 30.0$ is that this sample has less amount of $\text{SiO}_2$, which prevents oxygen from diffusing into the $\text{Fe}_2\text{O}_3\gamma\text{TiO}_2$ rich phase, than the other samples.

The peaks of all the wire samples contained both spinel and $\alpha\text{-Fe}_2\text{O}_3$ phases. The wire sample is easy to oxidize compared with the bulk one, because the wire sample has larger specific surface area than bulk one. The relative peak intensity of $\alpha\text{-Fe}_2\text{O}_3$ phase in $x = 30.0$ wire sample is obviously higher than the other ones, indicating that the more amount of iron ion in this sample is oxidized than that in the other ones. This is due to less amount of $\text{SiO}_2$ same as the bulk samples.

3.2. Magnetic properties

The magnetization curves of the bulk and wire samples are shown in Figure 2. Table 1 summarizes the results of the present magnetization measurements: magnetization at maximum applied magnetic field: 15 kOe, $M_s$, residual magnetization, $M_r$ and coercive force, $H_c$. The $M_s$ of both bulk and wire samples increased with increase of Fe-Ti content, $x$. Since the $M_s$ of sample is not proportional to the amount of $x$, this is due not only to the increase of the amount of spinel phase precipitated in the $\text{Fe}_2\text{O}_3\gamma\text{TiO}_2$-rich phase, but also to strengthening exchange interaction between iron ions. Their $H_c$ decreased with increasing $x$. This decrease of $H_c$ can be considered to arise from some difference of magnetic domain structure in the samples.

In the samples of $x = 15.0$ and 22.5, the $M_s$ and $M_r$ of the wire samples are higher than those of bulk samples. This difference of magnetic properties is most likely due to difference of cooling rate between the bulk and the wire samples resulting in change of the amount of precipitated spinel phase. On the other hand, the $M_s$ of the $x = 30.0$ wire sample lower than that of bulk one, because much larger amount of spinel phase changes to $\alpha\text{-Fe}_2\text{O}_3$. 
Spinel phase (Fe$_3$O$_4$-Fe$_2$TiO$_4$) and Hematite (α-Fe$_2$O$_3$) compositions. Figure 1. The XRD patterns of the melt-quenched bulk and wire samples with the composition of $x$Fe$_3$O$_4$-$y$TiO$_2$-(100-$x$-$y$)SiO$_2$+5Al$_2$O$_3$ [mol%, $y=x/3$].

Figure 2. The magnetization curves of the melt-quenched bulk and wire samples with the composition of $x$Fe$_3$O$_4$-$y$TiO$_2$-(100-$x$-$y$)SiO$_2$+5Al$_2$O$_3$ [mol%, $y=x/3$].

Table 1. Magnetization at maximum applied magnetic field: 15 kOe, $M_s$, residual magnetization, $M_R$ and coercive force, $H_c$, of the bulk and wire samples with the composition of $x$Fe$_3$O$_4$-$y$TiO$_2$-(100-$x$-$y$)SiO$_2$+5Al$_2$O$_3$ [mol%, $y=x/3$].

| $x$ mol% | Sample shape | $M_s$ [emu/g] | $M_R$ [emu/g] | $H_c$ [kOe] |
|----------|--------------|---------------|---------------|-------------|
| 15.0     | Bulk         | 12.43         | 6.355         | 1151        |
|          | Wire         | 16.01         | 8.488         | 983.7       |
| 22.5     | Bulk         | 18.98         | 9.697         | 1151        |
|          | Wire         | 20.82         | 10.13         | 557.4       |
| 30.0     | Bulk         | 29.40         | 13.49         | 528.3       |
|          | Wire         | 24.81         | 10.44         | 435.9       |
3.3. Internal texture

The SEM photographs of the bulk and the wire samples are shown in Figure 3. The bright and dark areas are attributed to Fe$_3$O$_4$-TiO$_2$-rich and SiO$_2$-rich phases, respectively, because of the difference of the emission efficiency of secondary electrons. The microstructures in the bulk samples consist of grains of SiO$_2$-rich phase dispersed in a matrix of Fe$_3$O$_4$-TiO$_2$-rich phase, which was formed by nucleation-growth process. The grain size of SiO$_2$-rich phase and the area of Fe$_3$O$_4$-TiO$_2$-rich matrix increase with increase of Fe-Ti content. On the contrary, the wire samples had needle-like SiO$_2$-rich phases oriented in the direction of elongation in parallel. Such a distorted phase-separation texture has a possibility to introduce anisotropy in the glass-ceramics [16].

![SEM photographs of the bulk and wire samples](image)

(a) Bulk sample

(b) Wire sample

Figure 3. SEM photographs of the melt-quenched bulk and wire samples with the composition of $x$Fe$_3$O$_4$-$y$TiO$_2$-(100-$x$-$y$)SiO$_2$+5Al$_2$O$_3$ [mol%, $y=x/3$].

4. Summary

The glassy composite magnetic material with needle-like phase-separation texture was obtained by quenching the two-immiscible phase-separated melt in the Fe$_3$O$_4$-TiO$_2$-SiO$_2$ ternary system. The precipitated crystalline phase was mainly the spinel phase of Fe$_3$O$_4$ or the Fe$_3$O$_4$-TiO$_2$ solid solution. In the sample with lower SiO$_2$ concentration, the larger amount of $\alpha$-Fe$_2$O$_3$ phase was precipitated. The texture formed by nucleation-growth process that consisted of the Fe$_3$O$_4$-TiO$_2$-rich and SiO$_2$-rich phases was observed at the bulk samples, and the SiO$_2$-rich phases in the wire samples were elongated. The direction of the elongated texture was parallel to that of elongation of the melt. All the samples showed ferromagnetic properties on their magnetization curves. The saturated magnetization increased and the coercive force decreased with increase of Fe-Ti content. It is thought that large amount of spinel phase was precipitated and that the magnetic domain structure changed from single magnetic domain to multiple one with increase of Fe-Ti content in the sample.
Acknowledgements
This work was supported by "Academic Frontier" project for private universities: matching fund subsidy from MEXT (Ministry of Education, Culture, Sports, Science and Technology), 2006-2010.

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