Magnetic Properties of Glass Ceramic in Fe₃O₄-MnO₂-SiO₂ System

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Abstract. The magnetic glass-ceramics was prepared by a melt-quenching method with the phase-separated melts in two-liquids stable immiscibility region of Fe₃O₄-MnO₂-SiO₂ system. The obtained glass-ceramics had spinel single phase of Fe₃O₄-MnO₂ solid solution, and showed ferromagnetic properties. The saturated magnetization became a maximum by adding a small amount of MnO₂ with low coercive force. These properties of both high magnetization and low coercive force by Mn doping are very effective to realize the magnetic materials for the hyperthermia treatment.

1. Introduction
The application of magnetic materials has been widely spreading, nowadays. As we have already mentioned in the previous work [1], hyperthermia treatments of tumors using ferro-, ferri- or superparamagnetic plate, needle or particles are one of the treatments for cancer [2-8]. As the basic study of the magnetic materials for such an objective, we have investigated the phase-separated glass-ceramics in Fe₃O₄-TiO₂-SiO₂ system prepared by a melt-quenching method because the melt-quenching process is feasible to control the shape of material such as a wire and a droplet and the phase separation texture has advantageous to protect the magnetic fine crystals against chemical reaction by a silica-rich glass phase. The obtained glass-ceramics showed ferromagnetic and electric conductive properties [1].

In magnetic oxide materials, a magnetic hysteresis loss is dominant origin of a generation of heat for the hyperthermia treatment. Thus, both a large hysteresis loop of a ferromagnetic material and a high frequency of an applied magnetic field are desirable characters and conditions to generate a large amount of heat. However, a high applied magnetic field with a high-frequency may give adverse effects to patient’s health. Thus, the magnetic materials should have large saturated magnetization and appropriately low coercive force to realize an enough heat generation for the hyperthermia without trouble to a patient’s health.

On the other hand, the manganese doped ferrite is reported to show a relative high magnetization among various ferrites [9, 10]. Furthermore, both Fe₃O₄-SiO₂ and MnO₂-SiO₂ systems have stable immiscibility region above their liquidus temperatures [11, 12]. Therefore, in this study, we prepared the magnetic glass-ceramics in the Fe₃O₄-MnO₂-SiO₂ system by use of a melt-quenching technique. The precipitated crystalline phase, the internal texture and the magnetic property of the melt-quenched samples were examined.
2. Experimentals

In the compositions of \((40-x)\text{Fe}_3\text{O}_4-x\text{MnO}_2-60\text{SiO}_2+5\text{Al}_2\text{O}_3\) (mol\%, \(x=0, 8, 16, 24\)), the starting raw materials of \(\alpha\text{Fe}_2\text{O}_3\), \(\text{MnO}_2\), \(\text{SiO}_2\) (\(\alpha\)-quartz), \(\text{Al}_2\text{O}_3\) (corundum) were mixed by ball-milling for 24 hours with ethanol. After drying the mixture of raw materials, the obtained powders were molded into a rod shape by use of a cold isostatic press, and the rods were sintered at 1200 °C for 12 hours in air. The sintered samples were melted for 3 minutes in air by use of an infrared imaging furnace (ULBAC, PRC MR-H500) and subsequently quenched.

The crystalline phases in the melt-quenched samples were analyzed by a powder X-ray diffraction (XRD, SHIMADZU, XRD-6100). The magnetic properties of the samples were evaluated from their magnetization curves, which were measured 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. Result and discussion

3.1. Crystalline phase

The XRD patterns of the melt-quenched samples are shown in Figure 1. The sharp diffraction peaks of each sample were identified as those from spinel phase of \(\text{Fe}_3\text{O}_4\) and/or \(\text{Fe}_3\text{O}_4-x\text{MnO}_2\) solid solution. In order to examine the effect of Mn doping on the crystal structure of ferrite, the changes of \(d\)-values of (220) and (311) diffraction peaks and the changes of integral intensities of those peaks against Si (111) as an internal standard substance were estimated and those results are shown in Figure 2. The former results indicate that both diffraction peaks linearly shifted to low angle with increase of the amount of \(\text{MnO}_2\). This result means that Vegard’s rule is applicable to \(\text{Fe}_3\text{O}_4-x\text{MnO}_2\) solid solution in this system, which was caused by replacing Mn ion with Fe ion. On the other hand, the later ones showed that the amount of precipitated spinel phase slightly decreased with increase of the amount of \(\text{MnO}_2\). This may indicate that the Fe atoms tend to form not spinel structure but glassy structure with \(\text{SiO}_2\) component as the amount of \(\text{MnO}_2\) increased.

![Figure 1. XRD patterns of the melt-quenched samples.](image)
Figure 2. Changes of the $d$ values; (a) and the diffraction intensities; (b) of precipitated spinel phase.

3.2. Internal texture

The SEM photographs of the melt-quenched samples are shown in Figure 3. The bright and dark areas are attributed to Fe-Mn-rich and SiO$_2$-rich phases, respectively. At the near-surface part of the melt-quenched droplet, the phase-separated texture was clearly observed and it became fine with increase of MnO$_2$ content, however, the phase separation texture was not observed inside of the melt-quenched droplets. On the other hand, the Fe-Mn rich phase was well-crystallized, especially in the samples of $x$=0 and 8 mol%. These results correspond to the result of the amount of crystalline phase in the XRD measurement shown in Figure 2 (b).

Figure 3. Cross-sections of the melt-quenched samples: the near-surface parts; (a) and the inside; (b).
3.3. Magnetic properties

The magnetization curves of the melt-quenched samples are shown in Figure 4. Figure 5 (a) shows the change of the magnetization at maximum applied magnetic field of $1.193 \times 10^6$ A/m and the amount of precipitated spinel phase. Figure 5 (b) shows the coercive force ($H_C$) and the crystallite diameter estimated from the diffraction peak (311) and Scherrer’s equation. As the amount of the precipitated spinel phase increased, the magnetization also increased. However, the sample of $x=4$ mol% exhibited the highest magnetization (saturated and residual). This result indicates that the magnetization increased by the small doping of Mn ions into spinel structure but decreased further doping of Mn ions. On the other hand, the $H_C$ and the crystallite size of each sample had some relationship, that is, a large crystallite size induced a low coercive force, which was caused by the formation of multiple magnetic domains in the large crystal. The obtained $H_C$ in this system is much lower than that of $\text{Fe}_3\text{O}_4$-$\text{TiO}_2$-$\text{SiO}_2$ system ($30\text{Fe}_3\text{O}_4$-$10\text{TiO}_2$-$60\text{SiO}_2$ mol%, $3.47 \times 10^4$ A/m), though the crystallite diameter, 36.5 nm is similar to those of the present samples.

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(40-x)\text{Fe}_3\text{O}_4-x\text{MnO}_2-60\text{SiO}_2
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![Figure 4. Magnetization curves of the melt-quenched samples.](image)

![Figure 5. Change of the magnetization and the coercive force with MnO$_2$ content.](image)
4. Summary

The magnetic glass-ceramics was prepared by quenching the two-immiscible phase-separated melt in the Fe$_3$O$_4$-MnO$_2$-SiO$_2$ system. The precipitated crystalline phase was spinel of Fe$_3$O$_4$ and/or the Fe$_3$O$_4$-MnO$_2$ solid solution. The formation of solid solution, in which Mn ions doped into spinel phase, was confirmed by the shift of the diffraction peak. In the sample of lower MnO$_2$ content, the larger amount of spinel was precipitated. The phase-separated texture was observed in all samples, and the crystallized texture was observed in the samples of lower MnO$_2$ content, especially. The saturated magnetization once increased and showed maximum at x=4 mol% and subsequently decreased with increase of the amount of MnO$_2$ content. The coercive force became smaller than that of Fe$_3$O$_4$-TiO$_2$-SiO$_2$ system. Though the coercive force did not change largely by changing the MnO$_2$ content, there was some relationship between coercive force and the spinel crystallite size, which caused by the formation of the multiple magnetic domain structure. These results show that the Mn doping in this system is very effective to realize the magnetic materials having both a high magnetization and a low coercive force, and that the obtained material will be possible to suppress the burden of patients in the hyperthermia treatment because of using lower applied magnetic field.

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