Magnetic properties of phase separated Fe$_3$O$_4$-TiO$_2$-SiO$_2$ glasses prepared from a two-liquids immiscible melt

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Abstract. The glassy composite materials were prepared by quenching the phase separated melts in two-liquids immiscibility region of Fe$_3$O$_4$-TiO$_2$-SiO$_2$ ternary system. The fine phase-separation textures which consisted of Fe-Ti rich phase and Si rich one were formed in the samples, and the precipitation of Fe$_3$O$_4$-TiO$_2$ solid solution was observed in the samples of the specific compositions. The samples containing Fe$_3$O$_4$-TiO$_2$ solid solution showed ferrimagnetic properties on their magnetization curves. In low Fe$_3$O$_4$-TiO$_2$ content, coercivity increased with increase of Fe$_3$O$_4$-TiO$_2$ content since the precipitated particles in the samples grew and had single magnetic domain. In high Fe$_3$O$_4$-TiO$_2$ content, the coercivity decreased with increase of Fe$_3$O$_4$-TiO$_2$ content because the magnetostatical interparticle interaction among the precipitated particles appeared. These results indicate that the magnetic properties of the composite materials owing to the crystalline phase and its size can be controlled by utilizing the phase separation in this system.

1. Introduction
Various properties of glasses and glass ceramics are widely utilized now-a-days, especially in optical and electronic applications. A phase separation is one of very popular phenomena of glasses., which influences on chemical, thermal and optical properties. There are two types of phase separation textures in the glasses, which are called as a binodal type and a spinodal one. A texture of the former type consists of discrete fine droplets of one amorphous phase and a continuous matrix of another phase, which is formed by a nucleation and growth process. Another texture of a later type consists of three-dimensionally interconnected two phases which is caused by a spinodal decomposition. The phase separation of glasses is a very useful phenomenon providing glassy composite materials because of its very particular fine texture, and have been applied for the preparation of the glasses having high chemical and thermal durability and the porous glasses in Na$_2$O-B$_2$O$_3$-SiO$_2$ system, which are well known as Pyrex$^®$ and Vycor$^®$ glasses, respectively. Recently, these particular glasses have been studied for the preparation of the phosphor [1-4], photocatalytic [5, 6] and magnetic materials [7, 8].

In a variety of silicate systems, a Fe$_3$O$_4$-SiO$_2$ binary system has wide composition range of liquid-liquid immiscibility, and the high temperature melt in that composition range separates spontaneously into SiO$_2$-rich glassy phase and Fe$_3$O$_4$-rich one. The later phase has a capability of showing ferromagnetic and semiconducting properties because of a precipitation of Fe$_3$O$_4$ (magnetite). When the phase separation in a Fe$_3$O$_4$-SiO$_2$ binary system utilized, the crystalline phase precipitated in the
Fe₃O₄-rich phase by some heat treatment was not magnetite but non-magnetic iron-silicate phase [7]. However, there are some reports that the glass ceramics containing magnetite crystalline phase in a CaO-Fe₃O₄-SiO₂ ternary system [9-11], and we also succeeded to prepare the phase separated glasses containing Fe₃O₄ in the same system [8].

On the other hand, Fe₃O₄-TiO₂ solid-solutions have been studied as a high versatility magnetic material [13-15]. Thus, we focused on Fe₃O₄-TiO₂-SiO₂ ternary system, which has been known to have a wide phase separation area [12]. In this ternary system, we expected that the ferrimagnetic Fe₃O₄-TiO₂ solid-solutions could be precipitated in phase-separated Fe-Ti-rich phase. In this study, the glass ceramics were prepared by using two-liquids immiscible melts in Fe₃O₄-TiO₂-SiO₂ ternary system and their magnetic properties were examined.

2. Experiments

The compositions of two-liquids immiscible melt were xFe₃O₄-yTiO₂-(100-x-y)SiO₂+5Al₂O₃ (mol%, x=5-30, y=x/3). The alumina of 5mol% was added to the composition in order to make the homogeneity of the composition higher, and to make the phase separation texture finer in the glasses. Starting raw materials of Fe₃O₄, TiO₂, SiO₂ and Al₂O₃ were mixed by ball-milling 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 ℃ for 12 h in the atmosphere. The sintered rod samples were melted for 4 min by use of an infrared imaging furnace (ULBAC, PRC MR-H500) and quenched by turning off the halogen lamp of the furnace.

The crystalline phases of the quenched samples were measured by use of a powder X-ray diffraction (XRD, SHIMADZU, XRD-6100). The crystallite size of the precipitates in the sample was determined by using the Scherrer’s equation [14]

\[ D = \frac{k\lambda}{\beta \cos \theta} \]

where \( D \) is the crystallite size, \( k \) is a shape function for which a value of 0.9 is used, \( \lambda \) is the wavelength of the radiation (Cu-Kα) and \( \theta \) is the angle of incidence. The value of \( \beta \) was determined from the full-width at half-maximum. The melt-quenched samples were cut vertically and polished, and their phase-separation textures were observed by use of a scanning electron microscope (SEM, JEOL, JSM-5800LV). Magnetic properties of the samples, which were grinded into powder, were evaluated from their magnetization curves, which were obtained by use of a vibrating sample magnetometer (VSM, Riken Denshi Model BHV-55).

3. Results and Discussions

3.1. Crystal and Texture

The XRD patterns of the melt-quenched samples are shown in Figure 1. The patterns showed diffraction peaks of a crystalline Fe₃O₄-TiO₂ solid solution and an amorphous halo due to SiO₂-rich glass phase, but in the compositions of higher Fe and Ti contents (x=25 and 30), a Fe₂O₃-TiO₂ solid solution phase also precipitated a little. The change of the crystallite size and the integrated intensity of the precipitates against the sample composition are shown in Figure 2. The inverted triangles display the crystallite size calculated from the (220) peak in the Fe₃O₄-TiO₂ solid solution phase, and the white and black circles show the integrated intensities obtained from the (220) peak in Fe₃O₄-TiO₂ solid solution phase and the (104) peak in the Fe₂O₃-TiO₂ solid solution one, respectively. In Figure 2, the intensity and the crystallite size of the Fe₃O₄-TiO₂ solid solution phase increased as the Fe₃O₄-TiO₂ content (x) increased up to x=15, and after that, the crystallite size saturated and the integrated intensity increased a little. On the other hand, the integrated intensity of the Fe₂O₃-TiO₂ solid solution phase steeply increased between x=25 and 30.
Figure 1. The XRD patterns of the melt-quenched samples \((x\text{Fe}_3\text{O}_4-y\text{TiO}_2-(100-x-y)\text{SiO}_2+5\text{Al}_2\text{O}_3\text{ mol\%}, x=5-30, y=x/3))\).

Figure 2. The change of the crystallite size and the integrated intensity against the sample composition, \(x\).

Figure 3. The SEM photographs of melt-quenched samples \((x\text{Fe}_3\text{O}_4-y\text{TiO}_2-(100-x-y)\text{SiO}_2+5\text{Al}_2\text{O}_3\text{ mol\%}, x=10-30, y=x/3))\): (A) \(x=10\); (B) \(x=15\); (C) \(x=20\); (D) \(x=25\); (E) \(x=30\).

The SEM photographs of the melt-quenched samples are shown in Figure 3. The fine textures which consisted of the bright and the dark sections were observed in the samples of \(x=10-30\), but such a phase-separated texture was not be observed at \(x=5\). Because of the difference of released secondary electron emission, the bright and the dark sections were attributed to the Fe-Ti rich phase and the Si rich one, respectively. In Figure 3 (A)-(B), the phase separation texture due to spinodal decomposition, which the Fe-Ti rich phase were intertwined to the Si rich one, was observed. On the other hand, in
Figure 3 (C)-(D), the discrete droplets of the Fe-Ti rich phase dispersed into Si-rich matrix owing to a nucleation and growth mechanism. These SEM photographs suggested that there was a possibility of the formation of the continuous magnetic phases in the samples of $x=10$-30. The phase diagram of the Fe$_3$O$_4$-TiO$_2$-SiO$_2$ ternary system and the classification of the phase separation texture based on the SEM results are shown in Figure 4. The diagonal area shows the two-liquids immiscible region to be expected from the binary systems [12], and the circle and the triangle points indicate the results of the examination of the phase separation.

![Figure 4. The phase diagram of Fe$_3$O$_4$-TiO$_2$-SiO$_2$ ternary system and the classification of the phase separation texture based on the SEM results. The diagonal area shows the two-liquids immiscible region to be expected from the binary systems.](image)

3.2. Magnetic Properties

The magnetization curves of the as-quenched samples are shown in Figure 5. The obvious magnetic hysteresis curves were observed for all samples except for $x=5$. The saturation magnetization of the samples at 15kOe linearly increased with their Fe$_3$O$_4$-TiO$_2$ content. The changes of the coercivity of the samples and the crystallite diameter of the precipitated solid solution in the samples with their compositions are shown in Figure 6. On the samples of low Fe$_3$O$_4$-TiO$_2$ content up to $x=10$, the coercivity increased with increasing of the crystallite size. However, on the samples of high Fe$_3$O$_4$-TiO$_2$ content more than $x=10$, the crystallite size almost became constant and the coercivity steeply decreased. The small crystallite size and the high coercivity at the low Fe$_3$O$_4$-TiO$_2$ content suggested the formation of single magnetic domain structure of the precipitated particle. This dependence of the crystallite size on the coercivity was very similar to the reported results of the Co-ferrite nanoparticles prepared by various processes [17, 18]. On the other hand, at the high Fe$_3$O$_4$-TiO$_2$ content, although the crystallite size became almost constant, the decrease of the coercivity still continued. This behavior indicated the existence of magnetostatical interparticle interaction because the amount of the precipitated magnetic particles increased.
Figure 5. The magnetization curves of the melt-quenched samples \((x\text{Fe}_3\text{O}_4-y\text{TiO}_2-(100-x-y)\text{SiO}_2+5\text{Al}_2\text{O}_3, \ x=10-30, \ y=x/3): (A) \ x=5; (B) \ x=10; (C) \ x=15; (D) \ x=20; (E) \ x=25; (F) \ x=30.

Figure 6. The changes of the coercivity of the samples and the crystallite diameter of the precipitated solid-solution in the samples with their compositions.

4. Summary
The glassy composite materials were prepared by quenching the phase separated melts in the two liquids immiscibility region of Fe\_3O\_4-TiO\_2-SiO\_2 ternary system. The two types of the fine phase separation textures which consisted of Fe-Ti rich phase and Si rich one were formed in the samples of different Fe\_3O\_4-TiO\_2 content. The different textures of the phase separation were formed due to spinodal decomposition or nucleation and growth process. The precipitation of the Fe\_3O\_4-TiO\_2 solid solution was also observed in the samples of Fe-Ti rich compositions. The samples containing this solid solution showed ferromagnetic properties on their magnetization curves. In low Fe\_3O\_4-TiO\_2 content, coercivity increased with increase of Fe\_3O\_4-TiO\_2 content since the precipitated particles in the samples grew and had single magnetic domain. In high Fe\_3O\_4-TiO\_2 content, the coercivity decreased with increase of Fe\_3O\_4-TiO\_2 content because the magnetostatical interparticle interaction among the precipitated particles appeared. These results indicate that the magnetic properties of the obtained composite materials owing to the crystalline phase and its size can be controlled by utilizing the phase separation in this system. Therefore, this process has a potential to prepare the composite materials which have various magnetic properties accompanied with high chemical durability, good mechanical properties and shape controllability due to a combination of the magnetic crystalline phase and the stable glassy matrix.

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