Morphology Control of Phase-Separation Texture by Elongation of Two-Liquids Immiscible Melt in Fe₃O₄–SiO₂ System

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Fe₃O₄–SiO₂系2液不混和融液の延伸による分相組織の形態制御

The existence of a liquid–liquid miscibility gap in Fe₃O₄–SiO₂ system has been reported. In this study, phase-separated glasses of 5 Fe₃O₄ 95SiO₂ (mol%) were prepared by melting sintered rods of the same composition at 1800°C (in immiscible region) using an infrared imaging furnace and, subsequently, quenching with elongation of the melts at a constant rate. The glass quenched without elongation exhibited a binodal type phase separation texture consisting of discrete spherical Fe₃O₄-rich particles. On the contrary, in the sample quenched with elongation, Fe₃O₄-rich particles were stretched and oriented along the direction of elongation.

The elongation of the particles in glasses was attempted in metal or metal halide colloids and oxide glass systems.6), 7) This process has been applied to the preparation of polarizing glasses. On the other hand, the elongation of phase separated glasses are reported in several oxide systems such as chemical-durable glasses and porous glasses, etc.8)–10) Considering the applications of phase separated glasses from other points of view, glassy composite materials derived from phase separation and subsequent precipitation of effective crystalline fine particles are expected to show high functional properties which are applicable to non-linear optical devices and advanced magnetic materials. Furthermore, when the morphology of phase separation can be controlled through some deformation process, the resultant composite material will appear anisotropic functions. The elongation of particles in glasses was attempted in metal or metal halide colloids and oxide glass systems.6), 7) This process has been applied to the preparation of polarizing glasses. On the other hand, the elongation of phase separated glasses are reported in several oxide systems such as PbO–B₂O₃ and a commercial borosilicate glass.8) Especially, for silicate systems, which generally show high viscosity, the direct quenching of two-liquid immiscible melts with elongation is effective crystalline fine particles are embedded in a SiO₂-rich glass matrix. In the previous our study on this system in miscibility gap, the morphology of phase separation and the fluctuations of the compositions were investigated.11) These phase-separated materials are promising as the base of new functional materials showing highly magnetic and magneto-electronic properties, because Fe₃O₄ (magnetite), which is crystallized from a Fe₃O₄-rich phase, shows both ferrimagnetic and semiconducting properties.

In this study, two-liquid immiscible melts in the system Fe₃O₄–SiO₂ were quenched with elongation. The morphology of phase separation in the quenched samples was examined by SEM observation. The relation between the condition of elongation and the resultant morphology of phase separation, and the controllability of the deformation of the phase separation texture were discussed.

1. Introduction
Glassy composite materials consisting crystalline fine particles and glass matrix have been investigated as high functional photonic and electro-magnetic materials for wide applications.1)–2) Phase separation is a widespread phenomenon in glassy materials and has been utilized for the preparation of various functional glasses such as chemical-durable glasses and porous glasses, etc.3)–5) Considering the applications of phase separated glasses from other points of view, glassy composite materials derived from phase separation and subsequent precipitation of effective crystalline fine particles are expected to show high functional properties which are applicable to non-linear optical devices and advanced magnetic materials. Furthermore, when the morphology of phase separation can be controlled through some deformation process, the resultant composite material will appear anisotropic functions. The elongation of particles in glasses was attempted in metal or metal halide colloids and oxide glass systems.6), 7) This process has been applied to the preparation of polarizing glasses. On the other hand, the elongation of phase separated glasses are reported in several oxide systems such as PbO–B₂O₃ and a commercial borosilicate glass.8) Especially, for silicate systems, which generally show high viscosity, the direct quenching of two-liquid immiscible melts with elongation is effective crystalline fine particles are embedded in a SiO₂-rich glass matrix. In the previous our study on this system in miscibility gap, the morphology of phase separation and the fluctuations of the compositions were investigated.11) These phase-separated materials are promising as the base of new functional materials showing highly magnetic and magneto-electronic properties, because Fe₃O₄ (magnetite), which is crystallized from a Fe₃O₄-rich phase, shows both ferrimagnetic and semiconducting properties.

In this study, two-liquid immiscible melts in the system Fe₃O₄–SiO₂ were quenched with elongation. The morphology of phase separation in the quenched samples was examined by SEM observation. The relation between the condition of elongation and the resultant morphology of phase separation, and the controllability of the deformation of the phase separation texture were discussed.

2. Experiments
The two-liquid immiscible melt of the composition: 5Fe₃O₄–95SiO₂ (mol%), was subjected to the elongation process. This composition was in the binodal region of phase separation and the resultant glass consisted of Fe₃O₄-rich particles and an SiO₂-rich matrix.11) Reagent grade α-quartz (SiO₂) and magnetite (Fe₃O₄) fine powders in the composition of 5Fe₃O₄–95SiO₂ (mol%) were mixed and calcined at 1350°C for 24 h in vacuo. The calcined powder was molded into a rod shape by use of a cold isostatic press (98 MPa). The rod samples were sintered at 1350°C for 24 h in vacuo. The sintered rods were melted at 2200°C (expected to be above miscibility gap) in the atmosphere by use of an infrared imaging furnace with 5.4 kW Xe lamp (Nichiden Machinery, FQ-50XS) in order to obtain a homogeneous single liquid phase. Subsequently,
the melt was cooled down to 1800°C and were held there for promoting phase separation. The temperature of the melting drop was measured by use of the monochromatic optical pyrometer with 5μm infrared ray (Japan Sensor, TSS-15 G) from the side of the melting drop.

Finally, the melt was quenched with elongation by two different methods as schematically illustrated in Fig. 1. In the method I, the center of a sintered rod was set in a focal point of the infrared imaging furnace and melted, and the melt was expected to elongate by falling down of the lower part of the sintered rod. In the method II, the tip of a sintered rod was melted, and the sintered rod with a melting drop was lowered a little and contacted with a silica glass rod. Immediately, the sintered rod was pulled up at the prescribed rate: 1.25, 2.50 or 5.00 mm·s⁻¹, and time: 1, 2, or 4 seconds.

The quenched samples were cut vertically and polished. The polished surfaces were etched with buffered HF solution (BHF, HF 2.0 mass% + NH₄F 17.0 mass%). Their morphology was observed by a scanning electron microscope (SEM; Hitachi, S-2050).

3. Result

The SEM photograph of the etched surface of the cross section in the sample which was melted at 2200°C-3min and immediately quenched without holding in the immiscibility region is shown in Fig. 2 (a), and that in the sample which was melted at 1800°C-3 min after melting at 2200°C and quenched without elongation is shown in Fig. 2 (b). There were no obvious etch pits due to phase separation in Fig. 2 (a). On the contrary, many discrete roundish etch pits less than 1μm in diameter were observed with some size distribution in Fig. 2 (b). Their mean diameter was 0.25 μm from an image analysis. Those pits are attributed to phase separated Fe₃O₄-rich particles formed by nucleation-growth process.

In the elongation operated by the method I, the center of the rod elongated at 1600°C due to the weight of its lower part, whereas, it could not elongate at 1800°C at all due to its high viscosity. On the contrary, at 1800°C, the melting part broke in due to its very low viscosity. Thus, it was very hard to control the elongation rate and time in this method.

On the other hand, the elongation of the melt was controllable in the method II. The SEM photographs of the etched surface in the samples elongated by various conditions in the method II are shown in Fig. 3. The samples subjected to the elongation had many needle-like etch pits which were oriented along the direction of elongation. The lengths of
the needle-like etch pits increased with elongation time. There were some discrete roundish etch pits on the extension line of the longer needle-like etch pits, except the disorderly scattered fine etch pits.

4. Discussion

4.1 Origins of various etch pits

The size distribution of discrete etch pits of the sample without elongation in Fig. 2(b) was caused by two reasons. One is due to the observation of a cut-off plane of the cross-section as schematically illustrated in Fig. 4. Another one is due to the Fe$_3$O$_4$-rich particles newly formed by secondary phase separation, that is, the iron oxide-rich particles were formed in the melt of previously formed SiO$_2$-rich phase during quenching.

From the results of the elongated samples by use of the method II, the discrete Fe$_3$O$_4$-rich particles were obviously deformed into needle-like shape. On the other hand, there are two kinds of discrete roundish etch pits in SEM photographs of the elongated samples. One is the disorderly scattered etch pits and another is those ordered on the extension line of longer needle-like etch pits. Former particles were formed by secondary phase separation during quenching as described above. The latter ordered etch pits are probably related to the deformation of particles because they are seen on the extension line of longer needle-like etch pits.

There are few papers discussed on the deformation of particles in immiscible liquids. Seward reported that the phase separation particles formed through metastable immiscibility were deformed by isothermal elongation at the temperature higher than its glass transition point under constant stress.\(^{8}\) He suggested from both experimental results and theoretical analysis that the degree of deformation of the particles depended on their size and that smaller particles were hard to deform, though his treated glass system had much higher viscosity of a minor phase (particles) than that of a major phase (matrix), which is in the reverse condition to the our sample. Gramespacher and Meissner reported the viscoelastic deformation of various polystyrene--PMMA blends with constant strain rates under isothermal conditions.\(^{13}\) They concluded that the aspect ratios of dispersing particles (polystyrene) increased with elongation and that the stretched particles were recovered into spherical shape after the viscoelastic recovery had been reached, in spite of their small interfacial energy.

From the discussions reported above, the stretched particles by elongation probably tend to return into spherical shape in order to make their interfacial energy minimum. On the other hand, the longer stretched particles are apt to break down into small particles because of the large expansion of their interface with the silica-rich matrix, and those small particles have tendencies toward recovering into spherical shape due to the same reason above. This indicates that the latter ordered etch pits were formed from one particle by breaking down and subsequent recovering into spherical ones during elongation as schematically illustrated in Fig. 5.

4.2 Elongation behaviors of phase separation texture

As the expression of degree of elongation, the aspect ratio of the particles is normally applied to such shape. However, it is hard for our samples to evaluate the width of these needle-like particles from SEM photographs because of their very thin widths. Thus, the degree of elongation was evaluated from the length of the needle-like etch pits, here. Furthermore, from above discussions of the origins of etch pits, the length of a stretched particle was measured by including the discrete roundish etch pits on its extension line.
Changes of the length distributions of the stretched particles with elongation rate and time were shown in Fig. 6. It seems that the length of the stretched particles become long and their distribution become wide as the elongation rate and time become fast and long, respectively.

The product of elongation rate and time is attributed to the apparent elongation distance of the melts. In order to examine the relation between the degree of stretching and the elongation distance, the mean lengths of the stretched particles prepared in respective conditions are plotted against the apparent elongation distance in Fig. 7. The mean length was in proportion to the elongation distance within the short elongation distance, whereas, the stretch of the particles was reduced as the apparent elongation distance became long. Since the results of different elongation rates were on the same curve in Fig. 7, the stretching behavior of the particles seemed to be independent on the elongation rate.

The direct proportion in the early stage of elongation in Fig. 7 indicates that the needle-like shape was formed by viscous flow or plastic deformation. The stretching behavior in the latter stage shows that the particles were stretched by viscoelastic deformation, apparently. Oxide melts and glasses at high temperature show viscous flow with Newtonian or various non-Newtonian behaviors; whereas the glasses in the vicinity of their glass transition temperature show viscoelastic or anelastic behaviors.\(^{14}\)

Fig. 6. Changes of the length distributions of the stretched particles with elongation rate and time.

Fig. 7. Change of the mean lengths of the stretched particles against apparent elongation distance.

The results of the method I suggest that our sample was able to elongate in the temperature range, \(1500^\circ\mathrm{C} < T < 1800^\circ\mathrm{C}\), though the elongated part was quenched by immediate leaving out of the focal point of the imaging furnace in our procedure. The softening point (viscosity of a glass: \(\log \eta = 7.65\)) of silica glass is \(1550^\circ\mathrm{C}\).\(^{39}\) The softening point of the major phase (matrix) of our sample may be close to that of silica glass because of its high silica content: \(95\ \text{mol}\%\), and the point was within above temperature range of the elongation. The viscosity of the minor phase (\(\text{Fe}_3\text{O}_4\)-rich particles) in this system is expected to be lower than that of the major phase (\(\text{SiO}_2\)-rich matrix) and the interfacial tension between the two liquid phases may be small because of their similar chemical compositions.

Considering from the above discussions including those from the reports,\(^8,13\) the spherical particles of phase separation were stretched by viscous flow in the early stage of elongation. The reduction of the stretching of the particles in the longer elongation as shown in Fig. 7 were caused by the restoring of the shape due to viscoelastic deformation or by the steep increase of viscosity due to leaving out of the focal point. It is hard to distinguish these effects because the deformation of the sample in this study went on under non-isothermal condition and, probably, uneven stress.

5. Conclusion

The immiscible melt in binodal region of \(\text{Fe}_3\text{O}_4\)-\(\text{SiO}_2\) system was elongated by use of the infrared imaging furnace. The quenched sample with elongation showed phase separation texture consisting of needle-like \(\text{Fe}_3\text{O}_4\)-rich phase that was oriented along the direction of elongation. Stretching of \(\text{Fe}_3\text{O}_4\)-rich particles by elongation caused this particular shape. The mean length was proportional to the elongation distance within the short elongation distance and was independent of the elongation rate; whereas the stretch of the particles was reduced as the apparent elongation distance became long. This suggests that the spherical particles grown by phase separation in binodal region were stretched by viscous flow in the early stage of elongation and the stretching in the latter stage was reduced by restoration due to viscoelastic behavior and/or the steep increase of viscosity.

The deformation and orientation of phase separation texture could be achieved in this process, though this deformation proceeded under non-equilibrium conditions. Therefore, the operated elongation process of two-liquid immiscible melts is capable of fabricating high-functional composite materials owing to the morphology control of phase separa-
tion texture.

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