Crystallization of (FeO, Fe₂O₃)-CaO-SiO₂ Glasses and Magnetic Properties of Their Crystallized Products

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(FeO, Fe₂O₃)-CaO-SiO₂ ガラスの結晶化と結晶化物質の磁気的性質

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The crystallization process of an Fe₂O₃ 40, CaO-SiO₂ 60 wt% glass was investigated as well as magnetic properties of the crystallized products, in order to reveal principles for obtaining ferrimagnetic and bioactive glass-ceramics useful as thermoseeds for hyperthermia of cancer. When the glass was heat-treated up to temperatures 700° to 950°C, magnetite particles were homogeneously precipitated in a CaO-SiO₂-based glassy and/or crystalline matrix. The diameter and content of the magnetite increased from 6 to 30 nm and 10 to 36 wt%, respectively, with increasing temperature of the heat treatment from 700° to 950°C. Above 1000°C, a part of the magnetite was converted into hematite (α -Fe₂O₃). The glass showed maxima in saturation magnetization and coercive force, 32 emu/g and 500 Oe, respectively, when heat-treated up to 950°C. The variation of the magnetization with heat treatment temperature could be well quantitatively interpreted in terms of the content of the magnetite, whereas that of the coercive forces could be explained only qualitatively in terms of the particle size of the magnetite. The coercive forces of the magnetite-containing glass-ceramics were much higher than those of the magnetite powders of the corresponding particle sizes which were prepared from aqueous solutions.

Key-words: Crystallization, Fe₂O₃-CaO-SiO₂ glass, Ferrimagnetic glass-ceramics, Magnetite, Hyperthermia

1. Introduction

It was previously shown by the present authors on the basis of investigations of bone-bonding mechanism of high strength bioactive glass-ceramic A-W^{1),2)} that P₂O₅-free CaO-SiO₂ glasses also bond to living bone forming an apatite layer on their surfaces in body environment.^{3),4)} It can be expected from these findings that bioactive and ferrimagnetic glass-ceramics precipitating magnetite (Fe₃O₄) in CaO-SiO₂ glassy matrices are obtained by crystallization of CaO-SiO₂ glasses containing appreciable amounts of Fe²⁺ and Fe³⁺ ions. Such glass-ceramics can be expected to be useful as thermoseeds for

hyperthermia of cancers, especially such as bone tumor, since this type of glass-ceramic will bond to living bone as well as with each other⁵⁾ to be fixed, when implanted around bone tumor in granular forms, and then the tumor will be locally heated up to temperatures above 43°C useful for cancer treatment by magnetic hysteresis loss, when placed under an alternating magnetic field. In the present study, in order to reveal principles for obtaining such bioactive and ferrimagnetic glass-ceramics, crystallization processes of (FeO, Fe₂O₃)-CaO-SiO₂ glasses were investigated as well as magnetic properties of their crystallized products.

Generally, tumor is more easily heated than the surrounding normal tissues, since blood vessel and nervous systems are poorly developed in the tumor, and cancer cell is easily killed by a heat treatment, since oxygen supply by the blood vessel is not sufficient in the tumor. Hence, hyperthermia is expected to be a most useful treatment of cancer which has no side effect.⁶⁾ Effective technique for local heating of cancer, however, has not been developed, especially for cancers, such as bone tumor, located at deep parts of body. Luderer et al. previously showed by animal experiments using glass-ceramic containing lithium ferrite (LiFe₅O₈) and hematite (α -Fe₂O₃) in an Al₂O₃-SiO₂-P₂O₅ glassy matrix that a ferrimagnetic glass-ceramic can be useful as a thermoseed for hyperthermia of cancer.⁷⁾ Their glass-ceramic was, however, not bioactive. Precipitation of magnetite from glasses has been studied by several workers.⁸⁾⁻¹⁰⁾ Crystallization of (FeO, Fe₂O₃)-CaO-SiO₂ glasses, however, has not been investigated.

2. Experimental

2.1 Preparation of glass

Powder mixtures about 30 g in amount of various compositions in the system Fe₂O₃-CaO-SiO₂ were prepared by reagent grade chemicals of Fe₂O₃, CaCO₃ and SiO₂. They were put into a platinum crucible and melted at 1550°C for 1 h in a MoSi₂ electric furnace. The melts were poured onto a stainless

steel plate at room temperature and pressed into a plate 1 to 2 mm thick. The cooled substance were examined by powder X-ray diffraction whether they contain crystalline phase or not.

2.2 Crystallization of glass

The glass plates obtained by the method described above were placed on a platinum sheet and heated at a rate of 5°C/min in a SiC electric furnace for crystallization. They were taken out from the furnace at various temperatures below 1100°C and allowed to cool in a laboratory atmosphere. The specimens heated up to temperatures above 850°C showed a change in color from black to red only at the surface. These specimens were used in the following experiments after their surface layers about 50 μm thick were removed.

2.3 Powder X-ray diffraction

The heat-treated specimens were subjected to powder X-ray diffraction using Ni-filtered CuKα ray. The kinds of the crystalline phases precipitated in the specimens were determined by referring to Data of Joint Committee on Powder Diffraction Standards.

The contents of the magnetite precipitated in the specimens were determined from the ratio of the intensity of 311 reflection of the magnetite to that of 111 reflection of calcium fluoride (CaF₂), which was added as the internal standard by 1 g to 5 g of the specimen. For the specimens precipitating both the magnetite and the hematite, the intensity of 311 reflection of the magnetite was obtained by subtracting the intensity of 110 reflection of the hematite from the intensity of the reflection at the corresponding diffraction angle, since both the reflections were overlapped. In this calculation, the intensity of 110 reflection of the hematite was assumed to be a half that of 104 reflection.¹¹⁾ The calibration curve for determination of the magnetite content was made using standard powder mixtures of the parent glass and the magnetite prepared by aqueous chemical reaction. The calcium fluoride was also added to the standard mixtures in weight ratio 1 : 5. The area of the observed reflection peak was taken as the intensity of the reflection.

The contents of the β-wollastonite (CaO·SiO₂) and the hematite precipitated in the specimens were only relatively determined from the ratios of the intensities of 400 reflection of the wollastonite and 104 reflection of the hematite, respectively, to 111 reflection of the calcium fluoride.

The lattice constant, *a*, of the cubic magnetite precipitated in the specimen was obtained by plotting *a* values calculated from interplanar spacing *d* values for 111, 311, 400, 422, 511, 440, 533 and 731 reflection against cos² θ and extrapolating linearly to cos² θ = 0.

Crystallite size and strain of the magnetite precipitated in the specimens were determined from broadening of reflection peaks of the magnetite us-

ing the following equation.¹²⁾

$$(B^2 - b^2) \cos^2 \theta = 4 \varepsilon^2 \sin^2 \theta + 0.81 \lambda^2 / t^2 \quad (1)$$

where *B*, *b*, *ε*, *λ* and *t* are the measured full width at half maximum intensity, the width due to the instrument, the strain, the wave length of X-ray and the crystallite size, respectively.

2.4 Mössbauer spectroscopy

The heat-treated specimens as well as the parent glass were subjected to Mössbauer spectroscopy at 300, 77 and 4.2 K, in order to investigate state of iron ions in them. Cobalt⁵⁷ in 10 mCi diffused into a copper matrix was used as radioactive source.¹³⁾ The γ rays were detected in a proportional counter filled with a gas mixture of Kr and CO₂. The data was accumulated in a 512-channel analyzer operating in the time-sequence-stage mode. The velocity calibration was obtained from the six-line hyperfine spectra of an iron foil.

2.5 Transmission electron microscopic (TEM) observation

The heat-treated specimens were crushed and sonically suspended in methanol. A few drops of the suspended solution were placed on an amorphous carbon film held by a copper microgrid mesh, and then observed under a transmission electron microscope (JEOL, JEM-2000FM).

2.6 Measurement of magnetic property

Magnetization (*M*) of the heat-treated specimens as well as the parent glass were measured as a function of the magnetic field (*H*) up to 10 kOe at room temperature using vibrating sample magnetometer (TOEI, VSM-2).

3. Results

3.1 Glass formation

Among the examined melts in the system Fe₂O₃-CaO·SiO₂, only those less than 40 wt% in Fe₂O₃ content formed glass containing no crystalline phase under the conditions described in section 2.1. In the following experiments, the glass containing the largest amount of Fe₂O₃, i.e. of the nominal composition Fe₂O₃ 40, CaO·SiO₂ 60 wt%, was used.

3.2 X-ray diffraction

Powder X-ray diffraction of the heat-treated specimens showed that the glass begin to precipitate the magnetite around 600°C and its content increases with increasing temperature reaching 36 wt% at 950°C as shown in Fig. 1. Above 950°C, the magnetite decreased with increasing temperature, while the hematite increased. The β-wollastonite began to precipitate around 700°C and maintained the content at a constant above 800°C.

The lattice constant, *a*, of the magnetite precipitated in the specimens was 8.39–8.40 irrespective of the heat treatment temperature, which almost coincided with the lattice constant 8.397 reported for the magnetite having the composition Fe₃O₄.¹⁴⁾

The crystallite sizes of the magnetite determined from Eq. (1) are shown in Fig. 2 as a function of

Fig. 1. Contents of crystalline phases as a function of heat treatment temperature.

Fig. 2. Crystallite size of magnetite as a function of heat treatment temperature.

heat-treated temperature. It increased with increasing temperature from about 6 nm at 700°C, through 35 nm at 950°C to 110 nm at 1100°C. The strains (da/a) of the magnetite determined from Eq. (1) were about 3×10^{-3} irrespective of the heat treatment temperature.

3.3 Mössbauer spectra

The Mössbauer spectra of the glass as-formed and heat-treated up to 700° and 950°C are shown in Figs. 3 to 5, respectively. Assignment of each peak based on the data reported for iron ion-containing glasses¹⁵⁾ and magnetite¹⁶⁾ is also shown in Figs. 3 to 5. Isomer shift, quadrupole splitting and hyperfine field of each spectrum are shown in Tables 1 and 2, as well as atomic fraction of each iron ion in different sites, which was estimated from intensity of the

Fig. 3. Mössbauer spectra at 300, 77 and 4.2 K of the glass as-formed.

Fig. 4. Mössbauer spectra at 300 and 77 K of the glass heat-treated up to 700°C.

respective spectrum. It can be seen from Fig. 3 that iron ions are present in the form of Fe^{2+} and Fe^{3+} in the as-formed glass, and Fe^{3+} ions sit in both the tetrahedral and octahedral sites. The atomic fraction of the Fe^{2+} , $\text{Fe}_{\text{tet}}^{3+}$ and $\text{Fe}_{\text{oct}}^{3+}$ ions were 0.11–0.16, 0.31–0.34 and 0.53–0.55, respectively. The iron ions showed paramagnetic spectra at 300 and 77 K, but weak Zeeman splitting due to magnetic interaction at 4.2 K. Those in the specimen heat-treated up to 700°C also showed paramagnetic spectra at 300 K but Zeeman splitting at 77 K. Most of the iron ions in the specimen heat-treated up to 950°C showed Zeeman splitting characteristic to the magnetite even at

Fig. 5. Mössbauer spectra at 300 and 77 K of the glass heat-treated up to 950°C.
M: Magnetite.

Table 1. Mössbauer parameters for the glass as-formed and heat-treated up to 700°C, and atomic fraction of Fe²⁺ and Fe³⁺ ions in tetrahedral and octahedral sites.

Specimen	Peak	Isomer Shift	Quadrupole Splitting	Assignment	Atomic fraction
As-formed at 300 K	I	0.38	0.83	Fe ³⁺ _{oct}	0.55
	II	0.34	1.44	Fe ³⁺ _{tet}	0.34
	III	0.88	2.46	Fe ²⁺	0.11
at 77 K	I	0.39	0.85	Fe ³⁺ _{oct}	0.53
	II	0.35	1.44	Fe ³⁺ _{tet}	0.31
	III	0.92	2.46	Fe ²⁺	0.16
Heat-treated up to 700°C at 300 K	I	0.37	0.57	Fe ³⁺ _{oct}	0.54
	II	0.34	1.24	Fe ³⁺ _{tet}	0.36
	III	0.73	2.58	Fe ²⁺	0.10

Table 2. Mössbauer parameters for the glass heat-treated up to 950°C and atomic fraction of Fe²⁺ and Fe³⁺ ions in different sites.

Temperature	Peak	Isomer Shift (mm/sec)	Hyperfine field (kOe)	Assignment	Atomic fraction
at 300 K	I	-	-	para	0.02
	II	0.72	462	Fe ²⁺ , Fe ³⁺ _{oct} (M)	0.52
	III	0.26	487	Fe ³⁺ _{tet} (M)	0.46
at 77 K	I	1.02	469	Fe ²⁺ (M)	0.23
	II	0.43	511	Fe ³⁺ (M)	0.77

(M): Magnetite

300 K. Only 0.02 atomic fraction of iron ions gave the paramagnetic spectra.

3.4 TEM observation

Transmission electron micrographs of the specimens heat-treated up to 700° and 950°C are shown in Fig. 6. The dark particles on the photographs were identified as the magnetite. Electronlucent matrix was identified as glassy phase and the β -wollastonite for the specimens heat-treated up to 700° and 950°C, respectively. It can be seen from Fig. 6 that the magnetite particles take a spherical form and are homogeneously dispersed in the matrices. The parti-

Fig. 6. TEM photographs of the glass heat-treated up to 700° and 950°C.

cle sizes of the magnetite were about 6 and 35 nm for the specimens heat-treated up to 700° and 950°C, respectively. These values almost coincided with the crystallite sizes obtained from the X-ray diffraction.

3.5 Magnetic property

A part of magnetization curves under magnetic field up to 10 kOe of the specimens heat-treated up to 700°, 800° and 950°C are shown in Fig. 7. Saturation magnetization M_s , that is defined as the magnetization at 10 kOe, and coercive force H_c of the heat-treated specimens are shown in Fig. 8 as a function of heat treatment temperature. Those for the specimens heat-treated up to temperatures below 800°C were also included in Fig. 8, although their magnetizations were not saturated even at 10 kOe. It can be seen Fig. 8 that the magnetization at 10 kOe increases with increasing heat treatment temperature from 2 emu/g at 600°C to 32 emu/g at 950°C, and then decreases. The coercive force increased with increasing heat treatment temperature from 20 Oe at 700°C to 500 Oe at 950°C, and then decreased.

Figure 9 shows $M-H$ curves measured under magnetic field up to 300 Oe, for the specimens heat-treated up to 700°, 800°, 850° and 950°C. It can be seen from Fig. 9 that the magnetic hysteresis loops under 300 Oe are much different from those under 10 kOe.

Fig. 7. A part of M - H curves under magnetic field up to 10 kOe of the glass heat-treated up to 700°, 800° and 950°C.

Fig. 8. Saturation magnetization M_s and coercive force H_c of the glass as a function of heat treatment temperature.

Fig. 9. M - H curves under magnetic field up to 300 Oe of the glass heat-treated up to 700°, 800°, 850° and 950°C.

4. Discussion

4.1 Glass structure

The melt of the nominal composition Fe_2O_3 40, $\text{CaO} \cdot \text{SiO}_2$ 60 wt% quenched on the stainless steel plate was identified as an amorphous state by the X-ray diffraction. It is, however considered to contain a certain amount of cluster in which magnetic interaction is caused between iron ions, since Mössbauer spectrum at 4 K showed Zeeman splitting. Coexistence of the Fe^{2+} with the Fe^{3+} ions in the glass is attributed to the partial reduction of the Fe^{3+} ions during the melting procedure at 1550°C.

4.2 Microstructure of crystallized product

X-ray diffraction and transmission electron microscopic observation showed that crystallized products of the glass take a structure in which spherical particles of the magnetite are homogeneously dispersed in a glassy matrix or a matrix consisting of glassy phase and β -wollastonite. The composition of the magnetite is speculated to be almost Fe_3O_4 from the lattice constant determined by X-ray diffraction, but a little rich in Fe^{3+} from Mössbauer spectra of the specimen heat-treated up to 950°C (see Table 2). Composition of the β -wollastonite of the matrix might be essentially $\text{CaO} \cdot \text{SiO}_2$, since both the Fe^{2+} and Fe^{3+} ions little enter into the lattice of the wollastonite. The composition of the glassy phase of the matrix is varied with the heat treatment temperature. That of the glassy phase in the specimen heat-treated up to 950°C is speculated to be essentially $\text{CaO} \cdot \text{SiO}_2$, since most of iron ions enter into the lattice of the magnetite and their only 0.02 atomic fraction are present in paramagnetic state (see Table 2). In this specimen, the magnetite takes 35 nm in size and 36 wt% in content.

4.3 Magnetic properties of crystallized product

The saturation magnetization of the crystallized products of the glass, which are shown in Fig. 8, are plotted against the content of the magnetite in them in Fig. 10. It can be seen from Fig. 10 that the saturation magnetization of the crystallized products almost linearly depends on the content of the magnetite. The saturation magnetization of the crystallized products extrapolated to 100 wt% of the magnetite is about 90 emu/g. This value almost coincides with the magnetization, 92 emu/g, reported for the magnetite of the composition Fe_3O_4 .¹⁷⁾ This means that the magnetite precipitated in the glass has almost same magnetization as that of the magnetite of the composition Fe_3O_4 and that the saturation magnetization of the crystallized products is almost determined by the content of the magnetite.

The coercive forces of the crystallized products of the glass are plotted against crystallite size of the magnetite in them in Fig. 11. Those reported for magnetite powders prepared from aqueous solutions¹⁸⁾ are also shown for comparison in Fig. 11. It can be seen from Fig. 11 that dependence of the

Fig. 10. Saturation magnetization M_s of the crystallized products of the glass as a function of content of the magnetite.

Fig. 11. Coercive force H_c of the crystallized products as a function of crystallite size of the magnetite, in comparison with those of magnetite powders prepared from aqueous solutions.

coercive force of the crystallized products on the crystallite size of the magnetite is similar to that of the magnetite powders, but that the values of the coercive force of the former are much higher than those of the latter. The dependence of the coercive forces of the crystallized products on the crystallite size might be interpreted in terms of magnetic domain structure, as in the case of the magnetite powders¹⁹⁾: i.e. at crystallite sizes smaller than 40 nm, the degree of ordering of the magnetic moment in the individual particles increases with increasing crystallite size, forming a well-ordered single domain at 40 nm, and at those larger than 40 nm, the number of the magnetic domain in the individual particles increases with increasing crystallite size, to decrease the coercive force.

The higher values of the coercive force of the crystallized products than those of the magnetite powders might be attributed to a larger stress applied to the magnetite particles and/or smaller magnetic interaction among the magnetite particles for the former. When the crystallized products was cooled to the room temperature, some stress might be applied to

Fig. 12. Area of magnetic hysteresis loop under magnetic field up to 10 kOe and 300 Oe, for the glass heat-treated up to various temperatures.

the magnetite particles, because of the difference in the thermal expansion coefficient between the magnetite and the matrix phase. Such internal stress might inhibit rotation of magnetic moment, increasing the coercive force.²⁰⁾ In the crystallized products, each magnetite particles are isolated by a non-ferrimagnetic matrix, hence the magnetic interaction among the magnetite particles, which decreases the coercive force,²¹⁾ might be not so large as in the magnetite powders. The coercive force, 500 Oe, of the specimen heat-treated up to 950°C, which contains almost single domain particles of magnetite, is very near to the coercive force, 550 Oe, calculated for the isolated single domain magnetite using the equation $0.96 K/M_s$, where K is constant of anisotropy, and -13×10^4 erg/cm³ for the magnetite.²⁰⁾

4.4 Heat-generating property of crystallized products

Generally, ferrimagnetic materials generate a heat in amount proportional to the area of the magnetic hysteresis loop and the frequency of the applied alternating magnetic field. Figure 12 shows the area of the magnetic hysteresis loop observed under the magnetic fields up to 10 kOe and 300 Oe, respectively, for the crystallized products, as a function of the heat treatment temperature. It can be seen from Fig. 12 that the amount of heat generation is appreciably decreased with decreasing magnetic field, and that the specimen heat-treated up to 950°C shows the maximum heat generation under 10 kOe, whereas the specimen heated up to 850°C does so under 300 Oe. This indicates that when a magnetic field as large as 10 kOe is available, the 950°C-heated specimen of the maximum coercive force is best as the thermoseed, whereas when only a magnetic field as

low as 300 Oe is available, the 850°C-heated specimen of a lower coercive force is better than the 950°C-heated specimen. Such a high alternating magnetic field as 10 kOe is not always available.

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