Published in final edited form as:

J Biomed Mater Res B Appl Biomater. 2012 July ; 100(5): 1198–1205. doi:10.1002/jbm.b.32684.

Effect of crystallization heat treatment on the microstructure of niobium-doped fluorapatite glass-ceramics

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Abstract

Our goal was to study the effect of heat treatment temperature and heating rate on the microstructure and crystalline phases and assess the domain of existence of sub-micrometer fluorapatite crystals in niobium-doped fluorapatite glass-ceramics for biomedical applications. Glass-ceramic specimens were prepared by casting and heat treatment between 700 and 1200°C using a fast or a slow heating rate. The microstructure was characterized by atomic force microscopy and scanning electron microscopy. Crystalline phases were analyzed by x-ray diffraction. AFM of the as-cast glass revealed that amorphous phase separation occurred in this system. XRD confirmed the presence of fluorapatite in all specimens, together with forsterite and enstatite at higher temperatures. Both heating rate and heat treatment temperature strongly influenced microstructure and crystallinity. A dual microstructure with sub-micrometer fluorapatite crystals and polygonal forsterite crystals was obtained when slow heating rates and crystallization temperatures between 950 and 1100°C were used. Needle-shaped fluorapatite crystals appeared after heat treatment above 1100°C. Fast heating rates led to an increase in crystal size. Heat treatment temperatures should remain below 1100°C, together with slow heating rates, to prevent crystal dissolution, and preserve a dual microstructure of finely dispersed sub-micrometer crystals without growth of needle-shaped crystals.

Keywords

fluorapatite; bioactive glass-ceramic; microstructure; crystallization; niobium

Introduction

Fluorapatite-containing glass-ceramics have been extensively studied. Glass-ceramics with combinations of hydroxyapatite, fluorapatite and various silicate phases such as mullite, fluorophlogopite, anorthite, diopside or wollastonite have been developed to match a wide array of opto-electronic and biomedical applications.^{1–8} The interest for hydroxyapatite and fluorapatite-containing ceramics for biomedical applications stems from their similarity in crystalline structure with biological apatites present in bones and teeth, and their excellent biocompatibility and bioactivity. Hydroxyapatite-coated implants for dental and orthopedic applications have been available for more than one decade. More recent studies have also reported on fluoridated hydroxyapatites as excellent candidates for implant coatings, exhibiting faster apatite deposition than pure HA, while showing similar alkaline

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phosphatase expression and cell attachment.⁹ Regardless of the application, the size and morphology of the fluorapatite crystals are of critical importance in achieving desired characteristics such as optical transparency, in the case of nano-scale crystals, or crystalline texture development in the case of needle-shaped crystals. In addition to opto-electronic applications, nanocrystalline glass-ceramics have generated considerable interest as novel bioactive materials capable of promoting enhanced osteoblast adhesion through nanotopography. Our previous work on fluorapatite glass-ceramics for biomedical applications demonstrated that a microstructure consisting of spherical nanoscale fluorapatite crystals could be tailored by addition of niobium oxide, while the undoped base composition exhibited micron-sized needle-shaped crystals.¹⁰ It was proposed that due to its small ionic radius and high ionic potential, niobium oxide promoted phase separation, which later enhanced crystal nucleation. This type of microstructure, in combination with the chemistry of fluorapatite was recently shown to promote human mesenchymal stem cell adhesion and osteoblastic differentiation on etched glass-ceramic discs, while polished control discs of identical chemistry led to poor cell attachment.^{11, 12} Several studies clearly demonstrated that human osteoblast attachment, spreading, proliferation and differentiation are significantly greater on nano-sized hydroxyapatite than on micron-sized hydroxyapatite.^{13,14, 15} Moreover, greater osteoblastic cell response was observed on nanosized fluorapatite-collagen composites than on hydroxyapatite-collagen composites.¹⁶ However, the domain of existence of this type of microstructure needs to be established. Processing of the glass-ceramic to manufacture intricate parts or scaffolds for bone graft substitutes may require a sintering step during which crystallization will occur. A thorough investigation of the crystallization behavior of this material is therefore needed.

Several studies have reported the existence of phase separation in fluorapatite-based glasses, which, in turn, strongly influences apatite crystal size and morphology.^{8, 17, 18} Moreover, the crystallization heat treatment conditions, particularly heat treatment temperature and heating rate are well known key factors in determining the final microstructure in glass-ceramic materials.¹⁹

The purpose of the present study was to investigate phase separation and vary heat treatment temperature and heating rate to establish the domain of processing parameters that yield submicrometer size fluorapatite crystals in niobium-doped fluorapatite glass-ceramics.

The long-term goal of the present study is to develop a fluorapatite glass-ceramic exhibiting nanosized isometric crystals that can promote bone formation through the development of surface nanotopography.

Materials and Methods

Specimen preparation

A fluorapatite glass-ceramic composition doped with 1 wt.% niobium oxide (Table 1) was prepared by mixing reagent grade oxides and carbonates, as previously described.¹⁰ The choice of dopant concentration was based on the reported microstructure and thermal properties of the glass-ceramic. About 10 wt.% excess fluorine was added to compensate for losses by volatilization. The batch ingredients were melted at 1525°C for 3 hours in platinum crucibles. After quenching in water, the glass frit was powdered and melted again at 1525°C for 3 hours. The molten glass was cast into a stainless steel mold to form cylindrical rods (12 mm in diameter; 60 mm in length). The rods were furnace-cooled from 685°C to room temperature and sectioned into discs (12 mm in diameter; 1.5 mm thick) using a low speed diamond saw. Specimens were heat treated in the temperature range 700–1200°C (50°C-increment) for 1h using either fast or slow heating and cooling rates. Fast

heating and cooling rates were achieved by using a pre-heated furnace. The slow heating rate applied was 2°C per minute, followed by furnace-cooling.

Differential thermal analyses (DTA) were performed on the powdered glass under nitrogen gas flow to determine glass transition and crystallization temperatures (Q600 DTA/TGA, TA Instruments). Analyses were performed at 20°C per minute up to 1200°C. Aluminum oxide (99.99%) served as reference standard.

Crystalline phases and percent crystallinity

The nature of the crystalline phases was investigated by x-ray diffraction (XRD) on powdered specimens. Scans were performed in the two-theta range 10–60 degrees, at a scanning rate of 1°C/min. (Miniflex II diffractometer, Rigaku Americas, λ CuK α = 1.5406 Å). For specimens containing solely fluorapatite, the percent crystallinity was determined after the establishment of a calibration curve using weighed amounts of commercially available fluorapatite (Clarkson Chromatography, Inc.) and parent glass powder. Patterns were analyzed using x-ray diffraction software (Jade 8, Materials Data Inc.). After K α -2 stripping and background fitting with a cubic-spline curve, the area above the background curve was measured. A linear fit (R-square=0.99) was obtained for the calibration curve. For specimens containing both fluorapatite and forsterite, the percent crystallinity was determined by quantitative stereology.

Microstructure, crystal dimensions and crystal number density

The microstructure of heat treated specimens was investigated by scanning electron microscopy (SEM) under secondary electron imaging (Sirion FEG, Philips Electron Optics). Specimens were polished to a 0.5 μ m-finish using a series of abrasives ending with diamond polishing pastes. They were etched with 1% aqueous solution of hydrofluoric acid for 10 to 60 seconds at room temperature, ultrasonically cleaned in ethanol, and gold coated prior to SEM examination. Crystal morphology (n =150) and crystal number density were characterized on digital micrographs using Image J processing software.²⁰ As indicated earlier, the percent crystallinity was determined by quantitative stereology on specimens containing both fluorapatite and forsterite.²¹ Phase separation was investigated by atomic force microscopy (AFM) on fractured and lightly etched surfaces of the as-cast glass and on specimens polished and further heat treated to 700°C.

Statistical methods

Results were analyzed by ANOVA and Tukey's test to detect statistically significant differences. A p -value of less than 0.05 was considered statistically significant.

Results

The as-cast glass was transparent but exhibited a light opalescence. Specimens remained opalescent after heat treatment up to 850°C for one hour but became opaque after heat treatment at 900°C and above.

Crystallization behavior

The DTA trace of the glass frit is shown in Figure 1. The glass transition temperature was 624°C. Three exothermic peaks were observed at 723, 855 and 1011°C.

X-ray diffraction of the glass powder after heat treatments simulating a DTA run to 905°C (above the first exotherm) revealed the presence of only fluorapatite. Forsterite was found in addition to fluorapatite after heat treatment to 975°C (above the second exotherm), while additional enstatite appeared after heat treatment to 1050°C (above the third exotherm).

X-ray diffraction patterns after heat treatment at various temperatures for one hour and with either a slow or a fast heating rate are displayed in Figures 2 and 3, respectively. There was no detectable crystallization in either as-cast glass or after heat treatment at 700°C, independently of heating rate. Fluorapatite ($\text{Ca}_{10}(\text{PO}_4)_3\text{F}_2$; PDF 015-786) was identified as the main crystalline phase after heat treatment at 750°C and up to 1200°C, independently of heating rate. Forsterite (Mg_2SiO_4 ; PDF 034-189) appeared after heat treatment at 850°C and higher with a slow heating rate, and at 950°C and higher with a fast heating rate. Enstatite (MgSiO_3 ; PDF 019-768) was found after heat treatment at 1050°C and up to 1150°C with a slow heating rate.

The total percent crystallinity determined from x-ray diffraction analyses is presented in Figure 4. There was a marked increase in crystallinity at 850°C with a slow heating rate and 1000°C with a fast heating rate. The percent crystallinity started to decrease at temperatures above 1100°C, independently of heating rate.

Microstructure, crystal dimensions and crystal number density

The evolution of the microstructure of the glass-ceramic as a function of heat treatment temperature with a fast heating rate is displayed in Figures 5. After heat treatment at 750 or 850°C, the microstructure consisted of densely packed spherical crystallites, 100 to 200 nm in diameter, but a very different microstructure was observed after heat treatment at 950°C, with more dispersed and larger crystallites (200–300 nm in diameter). Polygonal crystals (1 to 2 μm in length) were present after heat treatment at 1000°C and above, becoming progressively larger and less numerous as the heat treatment temperature increased. The final microstructure at 1200°C consisted of a few fluorapatite crystals of hexagonal section with a large amount of glassy matrix. Sub-micrometer crystallite dimensions and number density are summarized in Table 2. Generally mean crystallite size increased with temperature while the number density decreased. The most homogeneous crystallite dispersion was observed at 950°C and below.

The evolution of the microstructure of the glass-ceramic as a function of heat treatment temperature with a slow heating rate is shown in Figure 6. Similarly to what was observed with fast heating and cooling rates, a homogeneous and dense microstructure of sub-micrometer isometric crystallites (100 to 120 nm in diameter) was present after heat treatment at 750°C and up to 850°C (Figure 6A). Larger polygonal crystals (1 to 2 micrometers in diameter) appeared after heat treatment at 950°C, leading to a dual microstructure (Figure 6B). Heat treatment at higher temperatures led to a progressive decrease in the number density of sub-micrometer crystallites, associated with an increase in size. This was associated with a progressive disappearance of the dual microstructure. Only polygonal, prismatic or high aspect ratio needle-shaped crystals were observed after heat treatment at 1200°C (Figure 6E). Crystal dimensions and number density are summarized in Table 2. The same trends in crystal area and crystal number density were observed for both heating rates, but the decrease in crystal number density at the expense of the glassy matrix was much less pronounced with a slow heating rate.

The total percent crystallinity after heat treatment at 950°C and above was also measured on digital images using quantitative stereology. The results are presented in Figure 4 and are in good agreement with the results obtained by XRD analyses.

Atomic force micrographs of the as-cast glass (fractured surface) and after heat treatment at 700°C for one hour with a slow heating rate are shown in Figure 7A and B, respectively. The microstructure of the as-cast glass exhibited individualized islands of darker contrast (Figure 7A). Phase separated droplets (50–100nm in diameter) are clearly seen within the glass matrix after heat treatment at 700°C for one hour with a slow heating rate (Figure 7B).

Discussion

Differential thermal analyses (DTA) revealed the presence of three exothermic peaks at 812, 934 and 1087°C. The first exothermic peak at 812°C can be attributed to the crystallization of fluorapatite according to XRD analysis after heat treatment to 905°C. Meanwhile the second exotherm is attributed to forsterite (Mg_2SiO_4) and the third exotherm, to the crystallization of enstatite (MgSiO_3), as confirmed by XRD.

The opalescence present in the as-cast glass is a good indicator that phase separation occurred upon furnace-cooling of the glass melt from 685°C. This observation, together with the microstructure recorded by AFM on the as-cast glass (Figure 7A) and the fact that XRD did not reveal any detectable amount of crystallization, is consistent with glass in glass phase separation.²² Phase separation droplets (50–100 nm in diameter) later developed after heat treatment at 700°C for one hour (Figure 7B). The multiplication of these droplets between 700 and 750°C is illustrated in Figure 8, combining AFM and SEM images. Amorphous phase separation has been reported to occur in several apatite and fluorapatite-based glass-ceramic systems.^{1, 5, 7, 8, 19} It is the basis for the development of nanoscale fluorapatite crystals. Crystallization of fluorapatite occurs within the phase separated droplets and is limited by their size, up to 500 nm, as crystal growth is hindered by the depletion in key elements of the surrounding glassy matrix.^{8, 17} This leads to a microstructure of isometric fluorapatite crystals as opposed to needle-shaped crystals.⁸ It was also shown that depending on their composition and connectivity, phase separated droplets (PSDs) facilitate the crystallization of fluorapatite by lowering the activation energy for FAp crystal growth and by acting as heterogeneous nucleation sites. Although the glass composition studied in the present work differs from these previously reported fluorapatite and apatite glass-ceramic systems, we postulate that doping with niobium oxide acted by increasing the diffusivity in the glass and promoted glass in glass phase separation, with later crystallization of phase-separated droplets.

There was a good agreement between the percent crystallinity determined by XRD and that obtained from quantitative stereology measurements on scanning electron micrographs for heat treatment temperatures above 900°C (Figure 3). A fast heating rate led to increase in the crystallization temperature of fluorapatite, forsterite and enstatite of about 100°C, compared to slow heating rates. This resulted in lower values for the percent crystallinity. It is interesting to note that a discrepancy existed between the apparent microstructure of the glass-ceramic after heat treatment at 750°C or 850°C and the percent crystallinity as measured by XRD. As seen in Figure 5 and 6, a very dense microstructure consisting of sub-micrometer phase separated droplets (PSD) was observed by SEM, while the corresponding percent crystallinity was only between 20 and 40% as measured by XRD, and consisted exclusively of fluorapatite. These observations demonstrate that if some of the PSDs were crystallized at this stage, some of them remained amorphous. This is consistent with previous studies on fluorapatite glass-ceramics, showing the formation of primary Ca-P rich PSDs and secondary Al-P rich PSDs in the parent glass.^{3, 17, 23} The primary PSDs later crystallize into fluorapatite during further heat treatment, while the secondary PSDs remain amorphous. It was shown that the size of the fluorapatite crystals is limited by the size of the PSDs and an isometric shape is retained at lower temperatures and for slow heating rates because diffusion rates are low. Higher temperatures and fast heating rates permit anisometric growth of needle-shaped fluorapatite crystals of hexagonal section, as shown in Figures 5D and E.

Given the composition of the parent glass (Table 1), it can be calculated that the maximum amount of fluorapatite formed in this system is 25.9 wt. %. This is in good agreement with the measured percent crystallinity for heat treatments up to 900°C with a fast heating rate.

The further increase in total percent crystallinity observed from 950°C and above is interpreted as additional crystallization of forsterite and enstatite. The decrease in crystallinity after heat treatments at 1100°C and above is attributed to the dissolution of apatite isometric crystals.

The most striking effect of the different heating rates on the microstructure was observed at 950°C. A dual microstructure of isometric and polygonal crystals was obtained with a slow heating rate, while only isometric crystals with a two-fold increase in size were observed with a fast heating rate. This difference can be explained by the fact that slower heating rates may permit more efficient diffusion processes on a larger scale, leading to the crystallization of large polygonal forsterite crystals. Meanwhile, fast heating rates do not allow diffusion to occur on such a scale and the crystallization of a small amount of forsterite only begins at 950°C.

The crystallization of forsterite above 950°C makes this glass-ceramic system unique and has the potential to further enhance biological properties. Forsterite-containing ceramics have been shown to exhibit an excellent biocompatibility, with a high degree of osteoblast proliferation.²⁴ Recent work in our laboratory demonstrated that this niobium-doped fluorapatite glass-ceramic with dual microstructure of fluorapatite-forsterite crystals promoted human mesenchymal stem cell attachment, proliferation and differentiation.^{11, 12} The envelope of heat treatment schedules allowing the development of this type of microstructure appears compatible with a sintering cycle, which would be needed to process macroporous scaffold shapes.

Conclusions

Glass in glass amorphous phase separation occurred in this glass-ceramic system and determined the evolution of the microstructure after heat treatment, as the growth of fluorapatite sub-micrometer crystals was first limited by the size of the phase-separated droplets. Both heating rate and heat treatment temperature strongly influenced crystal size, crystal number density and crystalline phases.

Only slow heating rates and temperatures between 950 and 1100°C led to the development of a dual microstructure with sub-micrometer fluorapatite crystals and polygonal forsterite crystals. High heating rates led to an increase in size of the fluorapatite sub-micrometer crystals.

The temperature range for crystallization in this system should remain below 1100°C, together with slow heating and cooling rates, to prevent sub-micrometer crystal dissolution, and preserve a dual microstructure without growth of fluorapatite needle-shaped crystals.

Further work is underway to investigate the potential of this niobium-doped glass-ceramic as a synthetic macroporous scaffold material for bone grafts.

Acknowledgments

This work was supported by NIH-NIDCR R01 DE019972-01.

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Figure 1.
Differential thermal analysis trace of the as-cast glass.

Figure 2.
X-ray diffraction patterns as a function of heat treatment temperature with a slow heating and cooling rate.

Figure 3.

X-ray diffraction patterns as a function of heat treatment temperature with a fast heating and cooling rate.

Figure 4. Percent crystallinity as a function of heat treatment temperature and heating rate, as measured by XRD and quantitative stereology.

Figure 5.

Scanning electrons micrographs showing the microstructure of the glass-ceramic as a function of heat treatment temperature with a fast heating and cooling rate: (A) 750°C, (B) 950°C, (C) 1050°C, (D) 1150°C, (E) 1200°C.

Figure 6.

Scanning electrons micrographs showing the microstructure of the glass-ceramic as a function of heat treatment temperature with a slow heating and cooling rate: (A) 750°C, (B) 950°C, (C) 1050°C, (D) 1150°C, (E) 1200°C.

Figure 7.
Atomic force micrographs of A: as-cast glass (fractured and lightly etched surface); B: glass after heat treatment at 700°C for 1h (slow heating and cooling rates).

Figure 8.
Scanning electron micrograph after heat treatment at 750°C for one hour with matching scale inset showing atomic force micrograph after heat treatment at 700°C for one hour and phase separated droplets.

Table 1

Batch composition of the glass prepared (wt. %).

SiO ₂	30.5
MgO	13.8
Nb ₂ O ₅	1.0
CaO	14.4
Na ₂ O	2.3
K ₂ O	5.8
Al ₂ O ₃	15.9
F	4.9
P ₂ O ₅	11.4

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Table 2

Crystal size and number density as a function of heat treatment temperature and heating and cooling rates. (NI indicates crystals not individualized clearly enough to permit a count)

Temperature (°C)	Heating & cooling rates	Minor (µm)	Major (µm)	Area (µm ²)	Crystal number density (n per µm ²)
750	Slow	0.094±0.015	0.110±0.022	0.008±0.003 <i>a</i>	NI
850	Slow	0.109±0.018	0.128±0.025	0.011±0.004 <i>a</i>	NI
950	Slow	0.084±0.020	0.124±0.032	0.008±0.004 <i>a</i>	18.7±0.7 <i>f</i>
1000	Slow	0.123±0.021	0.174±0.050	0.017±0.007 <i>a</i>	11.3±0.4 <i>e</i>
1050	Slow	0.139±0.039	0.196±0.060	0.023±0.012 <i>a</i>	4.8±0.6 <i>d</i>
1100	Slow	0.184±0.046	0.303±0.120	0.046±0.026 <i>a</i>	2.6±0.4 <i>b</i>
1150	Slow	0.382±0.113	0.648±0.246	0.209±0.135 <i>c</i>	1.0±0.1 <i>a</i>
1200	Slow	0.446±0.117	0.717±0.282	0.266±0.145 <i>c</i>	0.5±0.1 <i>a</i>
750	Fast	0.115±0.025	0.168±0.060	0.016±0.009 <i>a</i>	NI
850	Fast	0.106±0.022	0.140±0.041	0.012±0.006 <i>a</i>	NI
950	Fast	0.199±0.034	0.280±0.088	0.045±0.019 <i>a</i>	6.5±0.1 <i>c</i>
1000	Fast	0.306±0.067	0.454±0.179	0.114±0.066 <i>b</i>	1.4±0.4 <i>b</i>
1050	Fast	0.338±0.062	0.514±0.191	0.141±0.069 <i>b</i>	1.0±0.2 <i>a</i>
1100	Fast	0.434±0.105	0.643±0.288	0.230±0.146 <i>c</i>	0.7±0.2 <i>a</i>
1150	Fast	0.492±0.099	0.791±0.301	0.315±0.161 <i>d</i>	0.4±0.1 <i>a</i>
1200	Fast	0.922±0.181	1.400±0.404	1.025±0.394 <i>d</i>	0.1±0.0 <i>a</i>

(Identical letters denote no statistically significant difference at *p*<0.05)