

T–T–T behaviour of bioactive glasses 1–98 and 13–93

Susanne Fagerlund, Jonathan Massera, Mikko Hupa, Leena Hupa*

Process Chemistry Centre, Åbo Akademi University, Turku, Finland

Available online 18 November 2011

Abstract

In this work crystallization kinetics of bioactive glasses 1–98 and 13–93 are discussed. Within a certain temperature–time window these glasses can be hot worked into various products without interfering with crystallization. The crystallization was studied isothermally by heating glass plates at different temperatures for different times. Phases in the samples were studied through XRD and SEM analyses. The nucleation-like curves and crystallization characteristics were measured with DTA. The temperature of maximum nucleation was measured for glass 1–98 at 725 °C and for 13–93 at 700 °C. The activation energy of crystallization of both glasses was 280 kJ/mol. The Johnson–Mehl–Avrami exponent and the SEM micrographs of the samples suggested surface crystallization. The primary crystalline phase was wollastonite. The growth rate of the crystallized surface layer was 1 order of magnitude higher in the plates of 1–98 than in 13–93. The results can be utilized to optimize the parameters in hot-working of the glasses.

© 2011 Elsevier Ltd. All rights reserved.

Keywords: Glass; Biomedical application; Thermal properties; Hot-working

1. Introduction

Bioactive glasses with their composition in the wollastonite primary field can be hot worked into various products without crystallization at carefully controlled time–temperature conditions.¹ These glass compositions can for example be sintered to porous implants or drawn into continuous fibres.^{1–5} Further, tissue engineering scaffolds with strut structure sintered of powdered fractions of bioactive glasses have been reported.^{6,7} The bioactive glass fibres have been tested as reinforcing components in different composite structures together with biodegradable polymers.⁸

Depending on the product, the glass forming operations take place within certain viscosity ranges. However, due to their low silica content and thus highly depolymerized structure compared to traditional glasses, bioactive glass melts crystallize easily at viscosity ranges typically applied in glass forming. For example, in the manufacture of porous bodies by viscous flow sintering of powdered glass above the glass transition temperature, too long residence times in the temperature range giving optimal viscosity might lead to extensive crystallization. The upper limit for the crystallization range is characterized by the liquidus temperature. In rotational viscometer the typical bioactive glasses crystallized at much lower viscosity values than utilized in

drawing of continuous fibres from glass melts.^{9,10} This implies that the viscosity at the liquidus temperature of bioactive glasses is much lower than the liquidus of conventional soda-lime glasses or fibreglasses. In practice, the crystal growth rate below the liquidus temperature is a limiting factor in glass forming. Thus, the strong tendency of bioactive glass melts to crystallize calls for a better understanding of their crystallization kinetics. For practical purposes the crystallization can be described with time–temperature–transformation (T–T–T) curves.

The aim of this work was to give detailed information on the T–T–T behaviour in heating of two bioactive glasses 1–98 and 13–93. The bioactivity of both glasses has been verified by *in vivo* studies. Amorphous porous implants sintered of the glasses have been shown to bond to rabbit femur.¹¹ Originally, their oxide compositions were developed in order to allow versatile hot working properties.^{11,12} However, in the working range both glasses are close to or partly within the temperature region in which they show high tendency to crystallize. The information obtained can be employed to adjust hot working parameters so that crystallization is avoided.

2. Experimental

2.1. Sample preparation

Bioactive glasses 1–98 and 13–93 were prepared from analytical grade reagents of Na₂CO₃, K₂CO₃, MgO, CaCO₃, H₃BO₃,

* Corresponding author. Tel.: +358 2 215 4563; fax: +358 2 215 4952.
E-mail address: leena.hupa@abo.fi (L. Hupa).

Table 1
Nominal glass composition (wt%).

Glass	wt%						
	Na ₂ O	K ₂ O	MgO	CaO	B ₂ O ₃	P ₂ O ₅	SiO ₂
1–98	6	11	5	22	1	2	53
13–93	6	12	5	20	–	4	53

CaHPO₄·2(H₂O) and Belgian quartz sand. The batches were melted in a platinum crucible for 3 h at 1360 °C, cast, annealed, crushed and remelted to ensure homogeneity. The nominal oxide compositions of the glasses are given in Table 1. The glasses were crushed and sieved to give the size range fraction 300–500 μm for the thermal analysis and cut to monolithic samples (20 mm × 10 mm × 5 mm) for the isothermal heat treatment.

2.2. Thermal analysis

The glass transition temperature T_g and the crystallization temperature T_p were determined by Differential Thermal Analysis (Mettler Toledo TGA/SDTA851^c) at various heating rates (10, 15, 20, and 30 °C/min). The measurements were performed on 50 mg samples with the particle size 300–500 μm in platinum pans in an N₂ atmosphere. T_g was taken at the inflection point of the endotherm, obtained by taking the first derivative of the DTA curve; T_p was taken at the maximum of the exothermic peak.

The activation energy E_c associated with the crystallization temperature was determined using the Kissinger equation (1) for T_p values measured at the different heating rates¹³:

$$\ln \left(\frac{q}{T_p^2} \right) = -\frac{E_c}{RT_p} + \text{constant}, \quad (1)$$

where q is the heating rate; T_p is the crystallization temperature measured at the different heating rates, and R is the gas constant.

The Johnson–Mehl–Avrami (JMA) exponent was determined using Eq. (2) proposed by Augis and Bennett¹⁴:

$$n = \frac{2.5}{\Delta T_{FWHM}} \frac{T_p^2}{E_c/R}, \quad (2)$$

where n is the JMA exponent and ΔT_{FWHM} is the full width at half maximum of the DTA peak. The JMA exponent gives information about the dimensionality of the crystal growth. The semi-quantitative, nucleation-like curve was determined using the method proposed by Marotta et al.¹⁵ The curve is based on heating samples up to several potential nucleation temperatures. The maximum of the exothermic peak in DTA curve was measured with (T_p) and without (T_p^0) an isothermal hold for 30 min at T , the potential nucleation temperature. A 20 °C/min heating rate was chosen to suppress the formation of nuclei during the heating of the glass. The nucleation-like curve (I_0) is then

obtained by plotting $((1/T_p) - (1/T_p^0))$ as a function of T , as shown by Eq. (3):

$$\ln(I_0) = \frac{E_c}{R} \left(\frac{1}{T_p} - \frac{1}{T_p^0} \right) + \text{constant} \quad (3)$$

where I_0 is the steady state nucleation rate and E_c is the activation energy for crystallization which represents the minimum amount of energy to initiate a reaction.

2.3. Isothermal heat treatment

Monolithic samples (20 mm × 10 mm × 5 mm) of the glasses were heat treated isothermally in the 600–1000 °C temperature range for 10 min to 8 h. The samples were inserted into an electric furnace on a graphite holder at a preset temperature. Experiments were conducted in N₂ atmosphere. The temperature in the furnace was controlled with a separate thermocouple within ±5 °C of the preset value. The heat treatment time was calculated from the moment the sample reached the preset temperature, i.e., roughly 15 min after inserting the sample into the furnace. After the treatment the samples were cooled in air. Two parallel samples were measured for each time point and for some selected points six parallel measurements were performed.

The cross-section of the plate was imaged with optical microscope (LEICA) equipped with a digital camera. Scanning electron microscope equipped with electron dispersive X-ray analyser (FEG-SEM, LEO 1530 Gemini from Leo/EDXA from Thermo Electron Corporation) was used to measure the average thickness of the crystallized layer and the composition of the phases in the samples. As the layers formed at the lower heat treatment temperatures and/or shorter times were not even, the thicknesses were measured in several locations for several plates. The values are given as arithmetical means with error bars indicating the minimum and maximum thicknesses.

Finally, the heat treated plates were ground to powder and the phase composition was analyzed using X-ray diffraction (X'pert by Philips, Cu α radiation, 40 kV, 30 mA, 5–60° 2θ, 0.8°/min). The diffractograms were analyzed using X'pert High Score, Powder Diffraction File database Data Sets 1–49 plus 70–86 (ICDD 1999). Powdered glasses of 1–98 and 13–93 prior to the heat treatment showed no signs of crystallization.

3. Results

3.1. The crystallization parameters with DTA

The DTA traces of 1–98 and 13–93 in Fig. 1, recorded at 20 °C/min heating rate, show an endothermic effect

Download English Version:

<https://daneshyari.com/en/article/1475071>

Download Persian Version:

<https://daneshyari.com/article/1475071>

[Daneshyari.com](https://daneshyari.com)