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DETERMINATION OF AVRAMI PARAMETERS OF HYDROXYAPATITE AND β-WOLLASTONITE IN BIOACTIVE PHOSPHOR – SILICA GLASSES

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Abstract

The properties of biologically active glasses in the system SiO_2–P_2O_5–MgO–CaO were studied. Crystalline hydroxyapatite (HA) and β-wollastonite (β-W) were used after heat treatment (1100°C).

The influence of the glass particle size (0.071–2.5 mm) and of glass powder ($d_{50}=15.1$ μm) on the behaviour of the products during differential thermal analysis was followed.

These analyses indicated that the β-W probably originates from surface nucleation, and HA from bulk nucleation.

The differentiation was confirmed by calculation of the Avrami parameters (n) with the Piloyan–Borchardt analytical method. For HA and β-W, the calculated values of n were 2.96 and 1.91. The surface-nucleated glasses exhibited predominant bidimensional crystal growth.

Keywords: Avrami parameters of HA and β-W, bioactive ceramics, HA and β-W crystallization

Introduction

It has been shown by many authors that a dense and homogeneous glassy system containing apatite and β-wollastonite (β-W) can be obtained when the glasses in the system SiO_2–P_2O_5–MgO–CaO are treated by an appropriate heating schedule [1–4].

Such glass-ceramics (A–W–GC) have already been used for implantation in clinical applications, and in vivo experiments demonstrated a good ability to interact with living bone [5–9].

Implants of A–W–GC type can be used especially under load-bearing conditions in the living body because they have good mechanical properties [10, 11].

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The processes of A–W–GC formation and crystal growth are not yet known in detail, however. In the present study, therefore, we focussed our attention on the influence of the glass particle size on the crystallization of hydroxyapatite (HA) and β-W. The courses of the DTA curves were analysed. The Avrami parameters for HA and β-W were then calculated by using the thermoanalytical data. The parameters relating to the shape and dimensionality of crystallite growth (*n=1 for 1-dimensional, n=2* for planar and $n=3$ for 3-dimensional growth) can be calculated from the slope of the Piloyan graph [12–16].

Experimental

Materials and preparation

A glass mixture of composition SiO_2 36.0, CaO 37.2, Na_2O 5.0, P_2O_5 14.3, MgO 3.0, B_2O_3 3.0 and Al_2O_3 1.5 (wt%) was prepared from reagent grade $CaCO_3$, Na_2CO_3, $CaHPO_4{\cdot}2H_2O$, MgO, H_3BO_3 and Al_2O_3; SiO_2 was added in the form of glass-making sand. The chemical composition of the dried sand was SiO_2 99.0, Fe_2O_3 0.025, TiO_2 0.15 and Al_2O_3 0.3 (wt%).

In the first step, the glass batch mixture was calcined in a covered platinum crucible at 1000°C for 5–6 h, and it was then melted at 1450°C for 2 h. The melt was poured out onto a stainless plate. The melt remaining in the crucible was cooled with cold water without allowing the water to contact the residue. Bulk glassy samples containing different particle size fractions, 2.5–2.0, 1.6–1.0, 1.0–0.63, 0. 63–0.315, 0.315–0.1 and 0.1–0.71 mm, and glass powder ($d_{50}=15.1$ μm) were used. The powder was prepared by pounding in an agate mortar.

Apparatus and procedure

DTA was performed by using the derivatograph 34–27 thermoanalyser at heating rates of 8.4, 9.4, 19.3 and 21.9 deg·min^{-1}.

Thermoanalytical data for calculation of the Avrami parameters were obtained from DTA curves recorded at heating rates of 8.4, 9.4, 19.3 and 21.9 deg·min^{-1} and by using glass powder with $d_{50}=9.35$ μm, prepared by milling glasses in a Fritsch planetary mill (Pulverisette 5) with alumina balls in isopropanol medium.

The Avrami parameters were calculated by using the following data: T_p = maximum temperature of exothermic crystallization peak, T_i=temperature at decisive point of exothermic peak, ΔT_i=deviation from DTA baseline at decisive point of exothermic peak, T_o=starting temperature of exothermic peak, and β=heating rate used.

The crystalline phases were identified by using a Dron 20 X-ray diffraction analyser.

Results and discussion

The DTA curves recorded for biologically active glasses with different particle sizes are compared in Fig. 1. The second exothermic peak, relating to β-W crystallization [11], shifts to higher temperature with increasing glass particle size, from 908°C for the glass powder to 1025°C for the 2.5–2.0 mm fraction. No further exothermic peak was found for the bulky glass sample.

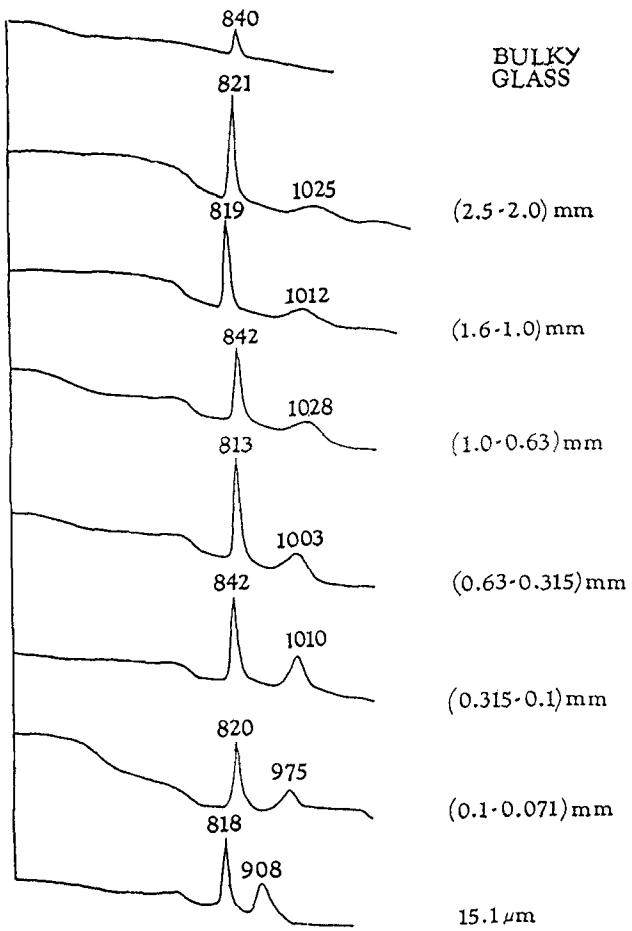

Fig. 1 DTA - curves of bioactive phosphor-silica glasses with different particle size used ($\beta = 9.4$ deg·min^{-1})

Before the two crystallization peaks (HA and β-W), no crystalline phase were confirmed by X-ray diffraction analysis. The recorded thermal effects could therefore be associated with the glass transformation of the metastable separated glassy matrix.

A comparison of the bioactive glasses as concerns their DTA curves is shown in Fig. 2. Four different heating rates were used. The DTA curves were corrected with the use of TAS software [17, 18].

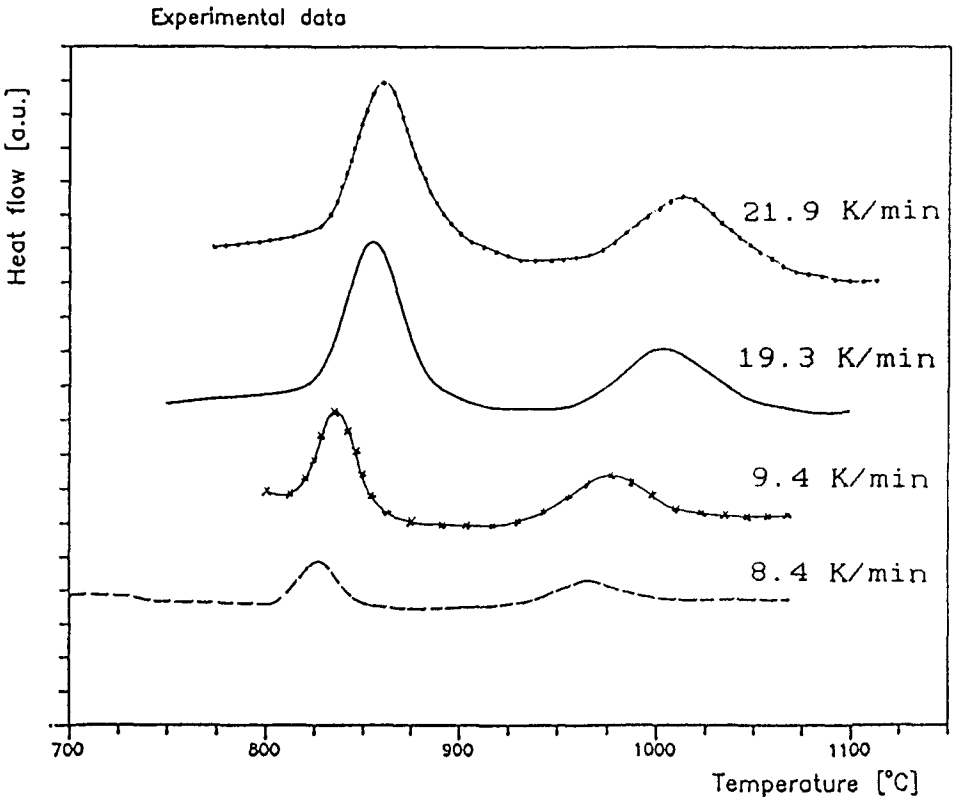

Fig. 2 Comparison of corrected DTA curves

The Avrami parameters were calculated from the slopes of Piloyan–Borchardt plots.

In the first step, the activation energies (E) of HA and β-W crystallization were calculated from the thermoanalytical data by using different analytical methods (Table 1).

The E values were calculated by four different analytical methods. The method of Marseglia was used after calculation of the Avrami parameters (Table 2).

Table 1 Analytical methods used for calculation of the kinetic parameters E and n

Analytical method	Equation	Slope	Reference
Augis–Bennett	$\ln\beta / (T_p - T_o) = f(1 / T_p)$	$-E / R$	19
Ozawa	$\ln\beta = f(1 / T_p)$	$-1.052\,E / R$	19
Kissinger	$\ln(\beta / T_p^2) = f(1 / T_p)$	$-E / R$	15, 19, 20
Piloyan–Borchardt	$\ln T_i = f(1 / T_i)$	$-nE / R$	12, 16
Marseglia	$\ln(\beta / T_p) = f(1 / T_p)$	$-nE / R$	21

The activation energies found for HA and β-W crystallite growth are given in Table 2.

Table 2 Experimentally found E values for the HA and β-W crystallization

Analytical method	E / kJ·mol^{-1}	
	Hydroxyapatite	β–wollastonite
Augis–Bennett	254	242
Ozawa	303	273
Kissinger	319	285
Marseglia	975	560

The methods of Ozawa and Kissinger yielded rather similar activation energies for the two components.

The Avrami parameters were then calculated from the E values obtained by the Kissinger method; they are listed in Table 3. The activation energies E=319 kJ/mol (HA) and E=285 kJ/mol (β-W) were used as basis.

Table 3 The Avrami parameters for HA and β-W crystals decomposed by different heating rates

β / K·min^{-1}	n(HA)	n(β-W)
8.4	3.14	2.15
9.4	2.96	1.81
19.3	2.55	1.66
21.9	3.21	2.02

These results showed that precipitation of β-W crystals is limited to the outer surfaces, and only growth towards the interior is permitted. This phenomenon may worsen the mechanical properties of glass-ceramics of A–W–GC type. It is expected that a dense crack-free glass-ceramic of A–W–GC type is obtained

when the glass is pulverized and the glass powder compact is treated by an appropriate heating schedule.

The biological properties of this material should not be influenced.

Conclusions

1. The DTA curves indicate that hydroxyapatite originates from bulk nucleation, and β-wollastonite by nucleation on the surface.

2. As concerns the shape of the crystals, the calculated average Avrami parameters, n(HA)=2.96 and n (β-W)=1.91, agree with the results in point 1.

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Zusammenfassung Es wurden die Eigenschaften biologisch aktiver Gläser im System SiO_2-P_2O_5-MgO-CaO untersucht. Nach Wärmebehandlung (1100°C) wurden kristallines Hydroxylapatit (HA) und ß-Wollastonit (ß-W) verwendet.
Der Einfluß der Glaskorngröße (0.071-2.5 mm) und von Glaspulver (d_{50}= 15.1 m) auf das Verhalten der Produkte bei der DTA wurde beobachtet.

Diese Analyse ergibt, daß ß-W wahrscheinlich einer Oberflächenkeimbildung entspringt, HA dagegen einer Vollkeimbildung.
Diese Unterscheidung wurde durch die Berechnung der Avrami'schen Parameter (n) mit Hilfe der analytischen Methode von Piloyan-Borchardt bestätigt. Die berechneten Werte n für HA und ß-W betrugen 2.96 und 1.91. Die über Oberflächenkeimbildung entstandenen Gläser zeigen ein vorherrschendes zweidimensionales Kristallwachstum.