

Changes of the mechanical properties during the crystallization of bio-active glass-ceramics

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A bio-active glass-ceramic material containing hydroxy apatite was investigated. The crystallization of the material during continuous heating was found to take place in three steps. The kinetics of the crystallization processes as well as their dependence on the particle size of the powder sample was investigated. Changes in the microstructure during the crystallization were observed and the crystallized phases were identified. The local mechanical properties such as microhardness and probability of crack formation as well as their changes with advancing crystallization were determined. The changes in the microstructure were correlated with those of the mechanical properties. © 2000 Kluwer Academic Publishers

1. Introduction

Bio-active glass-ceramics show a close chemical resemblance to the bone material and fulfill the physiological requirements for implantation in the human body as prostheses. Bio-activity means that chemical bonds are formed at the interface between the implant and the host tissue. The requirements of the biocompatibility are as follows:

- mechanical properties such as hardness, fracture toughness, elasticity must be similar to those of the bone material;
- thermal properties such as thermal expansion, thermal conductivity of these materials must resemble those of the bone material;
- absence of adverse effects on surrounding tissue;
- absence of effects on free metabolic processes;
- long-term life expectancy [1].

Examples of bio-active glass-ceramics are glasses containing hydroxy apatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$, HA) crystals and fluor apatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$, FA) crystals, respectively [2]. These materials were tested in dental surgery.

In this paper results of mechanical and calorimetric measurements taken on a hydroxy apatite containing glass-ceramic material are presented. Changes of the mechanical properties during the crystallization were monitored and connected with those of the microstructure.

2. Experimentals

The material investigated was produced of powders of CaO (30–40), P_2O_5 (12–20), CaF_2 (0.1–0.4), MgO (2–8) and amorphous SiO_2 (35–45), by weight ratio*. The

powder mixture was melted at about 1450 °C, homogenized and then cooled to obtain a glassy material.

The heat effects during the crystallization processes were investigated by calorimetry. The measurements were carried out in a Differential Scanning Calorimeter (DSC) on the bulk material. The phases formed during the crystallization were identified by X-ray and electron diffraction. In addition, the amorphous starting material was pulverized and the powder particles obtained were separated by sieving into fractions of different particle sizes. This allowed the investigation of the particle size dependence of the crystallization processes. The DSC measurements were carried out under continuous purging with 6N purity Ar. The changes in the microstructure of the material were investigated by X-ray and electron diffraction as well as by transmission and scanning electron microscopy (TEM and SEM).

The local mechanical properties of the glass-ceramic were investigated by a Shimadzu DUH-202 dynamic microhardness tester on mechanically polished bulk samples in the as received amorphous state as well as after different annealings carried out in the DSC-apparatus. Mechanical investigations involved the measurement of the hardness distribution and of crack statistics, both characterizing the local mechanical properties of the material. The hardness distribution was determined on the basis of dynamical Vickers microhardness [3, 4]. During these tests a Vickers pyramid loaded at constant loading rate up to 50 mN penetrates the surface of the sample and the same rate is applied in the unloading period when the pyramid moves backwards. In the test the indentation depth is continuously registered and the Vickers microhardness can be determined.

* The material was provided by the Central Research and Design Institute for Silicate Industry, Budapest.

For characterization of the fracture properties of the material the statistics of the cracks starting out of the corners of the Vickers patterns was investigated. Investigating many Vickers patterns and assuming random crack initiation, the probability of crack formation can be approximated with the ratio of the number of the corners from which cracks start (N) and of the total number of the corners (N_0): $P = N/N_0$.

3. Results

3.1. Crystallization processes

On the basis of TEM and X-ray diffraction microstructural investigations the as received, unheated material was found to be fully amorphous. Fig. 1 shows the 10 °C/min linear heating DSC thermogram obtained on a bulk sample of about 60 mg mass.

By investigating the second heating of the same sample it was verified that the transformations are irreversible. In the thermogram of Fig. 1 three exothermal peaks were observed. According to the results of X-ray (see 3.2.1 point) and electron diffraction investigations these peaks can be associated with the following crystallization steps:

1. The peak appearing at 900 °C indicates the crystallization of hydroxy apatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$).
2. The peak at 1027 °C is connected with the formation of β -whitlockite ($\text{Ca}_3(\text{PO}_4)_2$).
3. The peak at 1083 °C corresponds to the formation of wollastonite (CaSiO_3).

The bulk material was milled and the powder was separated by sieving into fractions of different particle sizes to investigate the effect of the specific surface on the crystallization processes. A series of thermograms obtained under the same conditions as in Fig. 1 is shown in Fig. 2.

It can be seen that the variation of the specific surface does not influence the position and the shape of the first peak corresponding to the crystallization of hydroxy apatite. The peak associated with the formation of β -whitlockite is shifted towards lower temperatures with decreasing particle size. This shows that the formation of β -whitlockite is enhanced by the increase of the specific surface, indicating that the formation of β -whitlockite takes place preferentially by surface nu-

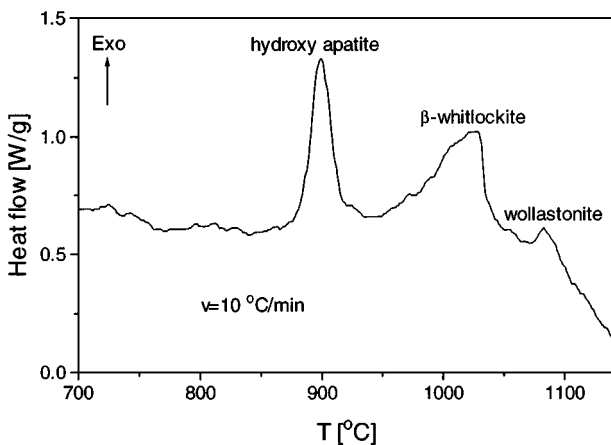


Figure 1 Thermogram of the bulk sample.

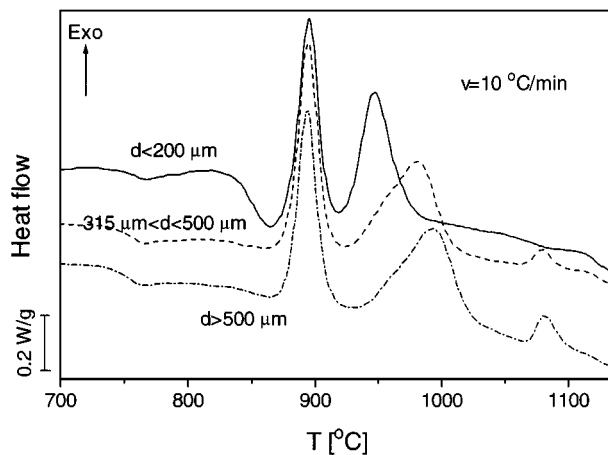


Figure 2 Three of the thermograms taken at different particle sizes.

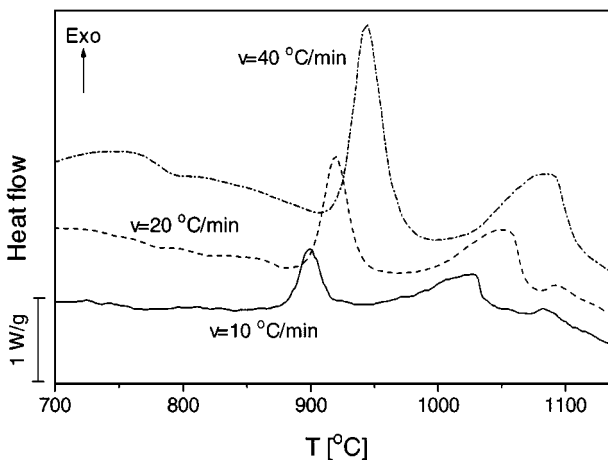


Figure 3 Three of the thermograms taken with different heating rates.

cleation. The location of the peak corresponding to the formation of wollastonite is not changed with the variation of the particle size, but its height is decreasing and finally it disappears with the refinement of the powder. This shows that the formation of the wollastonite crystals can be suppressed by the increase of the specific surface.

To investigate the kinetics of the crystallization processes thermograms at different heating rates were also taken on samples of the bulk material. A series of thermograms is shown in Fig. 3.

With increasing heating rates the peaks are shifted towards higher temperatures, furthermore the height of the peaks increases proportionally to the heating rate. The shift of the peaks is due to the thermally activated character of the structural transformations. The characteristic activation energy of the crystallization processes can be determined from the $\ln v = -1.052 \cdot E/R \cdot 1/T_p + c_1$ Ozawa-equation or from the $\ln v/T_p^2 = -E/R \cdot 1/T_p + c_2$ Kissinger-equation, respectively, both obtained from the JMAK theory of the reaction kinetics by applying some mathematical approximations [5]. Activation energies of 370 ± 1 kJ/mol and 308 ± 3 kJ/mol were obtained for the crystallization of hydroxy apatite and β -whitlockite in the bulk material, respectively. (The activation energy for the crystallization of wollastonite indicated by the 3rd peak could not be determined with acceptable accuracy.)

3.2. Investigation of the microstructure

3.2.1. Electron diffraction and X-ray diffraction

On the basis of the electron diffraction patterns obtained on the as received sample and on those heated to the temperatures of the characteristic peaks in the thermogram it was found that the as received sample is fully amorphous, but the other samples are partly crystallized. The different phases formed during the heat treatment were identified as mentioned in 3.1.

Fig. 4 shows the X-ray diffraction patterns of the samples after heating up in the calorimeter at 10 K/min to 900 °C (a), 1027 °C (b) and 1038 °C (c), respectively. Fig. 4a proves, that at 900 °C the dominant crystalline phase is HAP. The amount of the traces of wollastonite is negligible. According to Fig. 4b at 1027 °C β -whitlockite is appearing. Finally Fig. 4c indicates that at 1038 °C there are three crystalline phases: HAP, β -whitlockite and wollastonite. From the intensities of the X-ray lines the fraction of the different phases formed during the three different heating treatments can be determined approximately (Fig. 5).

It was found that at the temperature of the 1st peak nearly 70% of the sample is crystalline hydroxy apatite, the rest is composed of amorphous material and of a negligible amount of β -whitlockite and wollastonite. The fraction of the amorphous phase is slightly decreasing during the higher temperature heating treatments. At the temperature of the 2nd peak the amount of β -whitlockite is half of that of hydroxy apatite. At the 3rd peak, the fraction of wollastonite is about 10%, while the percentages of hydroxy apatite and β -whitlockite are equally about 35%.

3.2.2. TEM

On the TEM picture obtained on a sample heated to the temperature of the 1st calorimetric peak dendrites of hydroxy apatite with an average diameter of 2–3 μm were observed and amorphous material between the dendrites (Fig. 6).

From the diameter of the dendrites the distance between neighbouring nuclei can be estimated as 2–3 μm . The microstructure of the material heated to the temperature of the 3rd peak is quite different (Fig. 7).

Interweaving crystals of hydroxy apatite, β -whitlockite and wollastonite can be observed. The diameter of the crystallites is about 0.1–0.5 μm . The space where amorphous regions were observed previously is partially filled up by crystallized material. Above the temperature of the 3rd peak the crystals continue to grow: in the sample heated to 1155 °C and hold for 1 hour at this temperature (Fig. 8) crystal grains of about 3 μm diameter can be seen while within the crystals small inclusions surrounded by weak stress fields can be observed. It is worth mentioning that no pores or microcracks have been revealed in the TEM micrographs of the crystallized samples.

3.2.3. SEM

Comparing the SEM pictures obtained from the fracture surface of the as received sample with those following heat treatments the changes in the surface

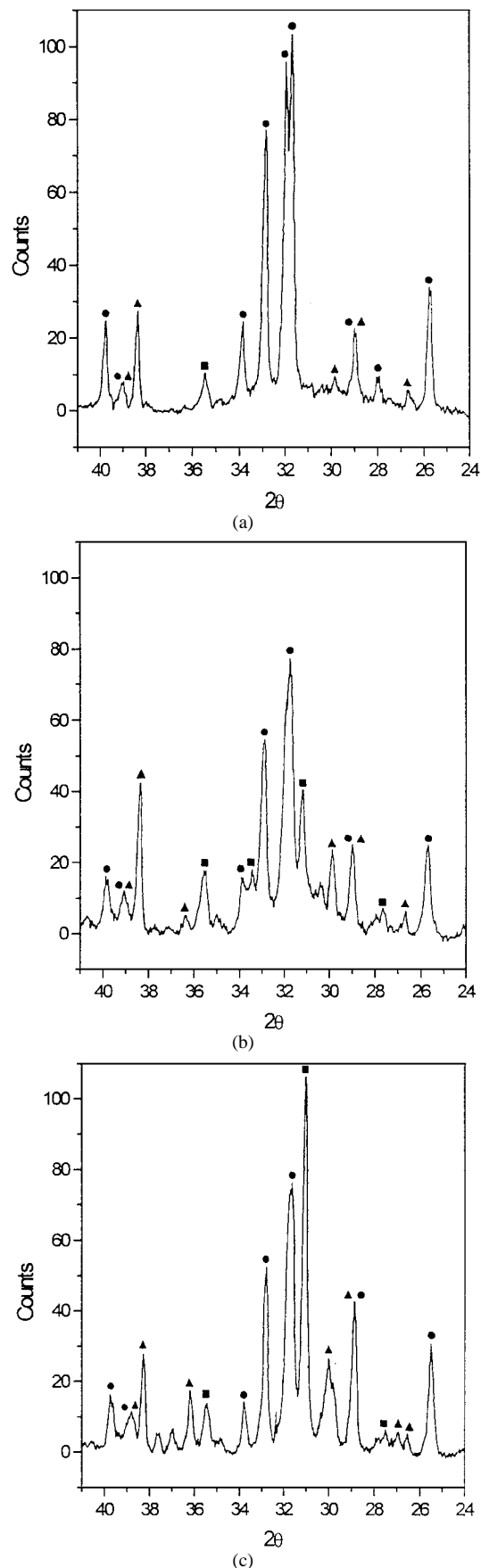


Figure 4 (a) XRD spectrum of a sample heated to the temperature of the 1st peak (●: HAP—ICDD—JCPDS 9-0432, ■: β -whitlockite—ICDD—JCPDS 6-0426, ▲: wollastonite—ICDD—JCPDS 43-1460); (b) XRD spectrum of a sample heated to the temperature of the 2nd peak (●: HAP—ICDD—JCPDS 9-0432, ■: β -whitlockite—ICDD—JCPDS 6-0426, ▲: wollastonite—ICDD—JCPDS 43-1460); (c) XRD spectrum of a sample heated to the temperature of the 3rd peak (●: HAP—ICDD—JCPDS 9-0432, ■: β -whitlockite—ICDD—JCPDS 6-0426, ▲: wollastonite—ICDD—JCPDS 43-1460).

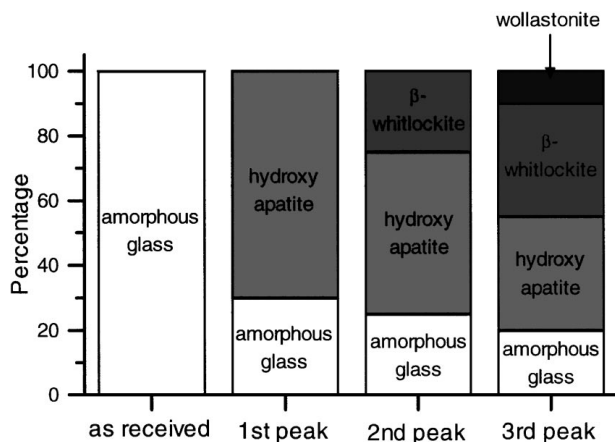


Figure 5 Composition of the as received sample and of the samples heated to the peak temperatures.

microstructure due to the crystallization can be seen. The fracture surface of the as received sample and that of the sample heated to the temperature of the 1st peak (Fig. 9) show a typical brittle fracture morphology with a few shell-like lines of break.

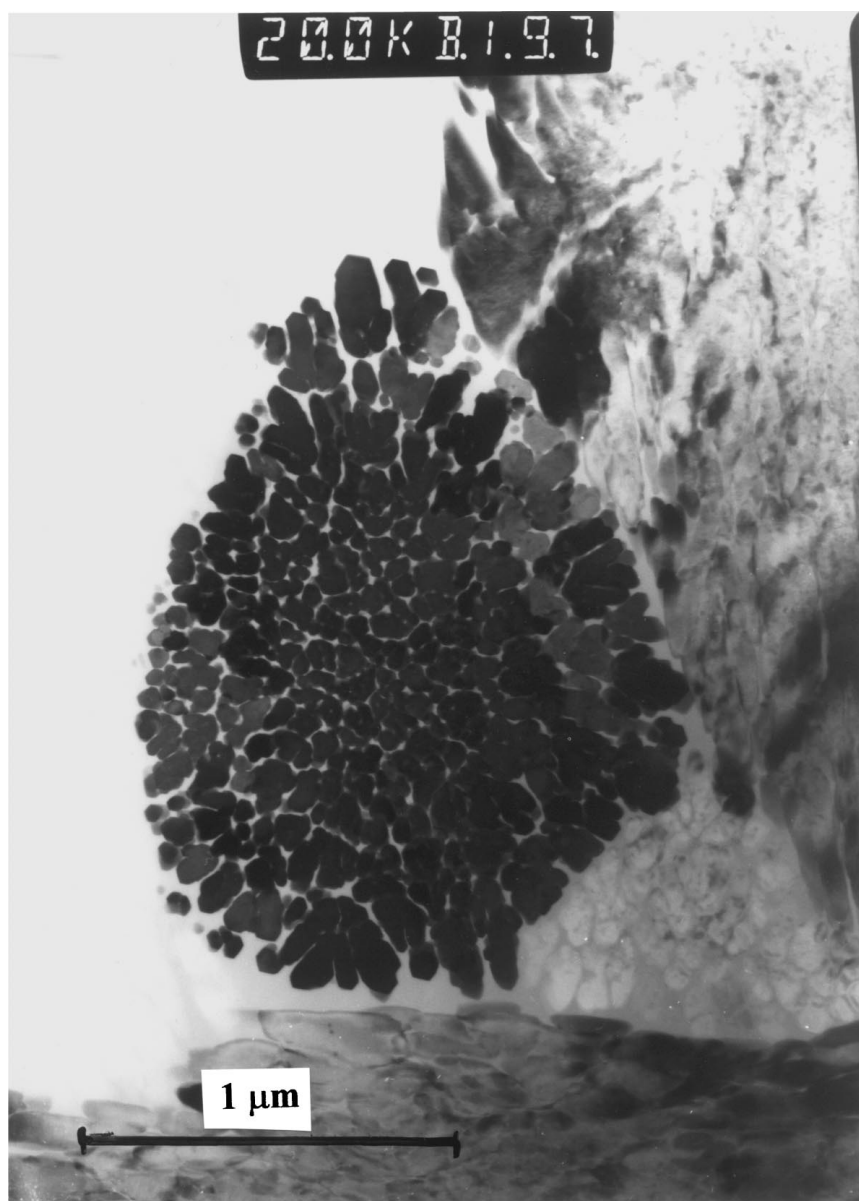


Figure 6 TEM micrograph of a sample heated to the temperature of the 1st peak.

At the temperature of the 3rd peak (Fig. 10) the surface is characteristic of ductile fracture and shows a varied “relief”.

Above this temperature the surface becomes more and more inhomogeneous: on the surface of a sample heat treated at 1155 °C for 1 hour (Fig. 11) grains of different shapes and sizes can be seen (the diameter of the spherical hydroxy apatite and β-whitlockite crystals is about 5–10 μm, the plate-like wollastonite crystals are larger than 10 μm).

3.3. Mechanical investigations

3.3.1. Microhardness

100 microhardness measurements were made on the as received sample as well as on samples heated to the temperatures of the calorimetric peaks. The indentation depth was continuously registered while the load was increased at a constant loading rate. The microhardness was determined by using the formula:

$$H_V[\text{GPa}] = 0.0378 \cdot \frac{F[\text{mN}]}{h^2[\mu\text{m}^2]}, \quad (1)$$

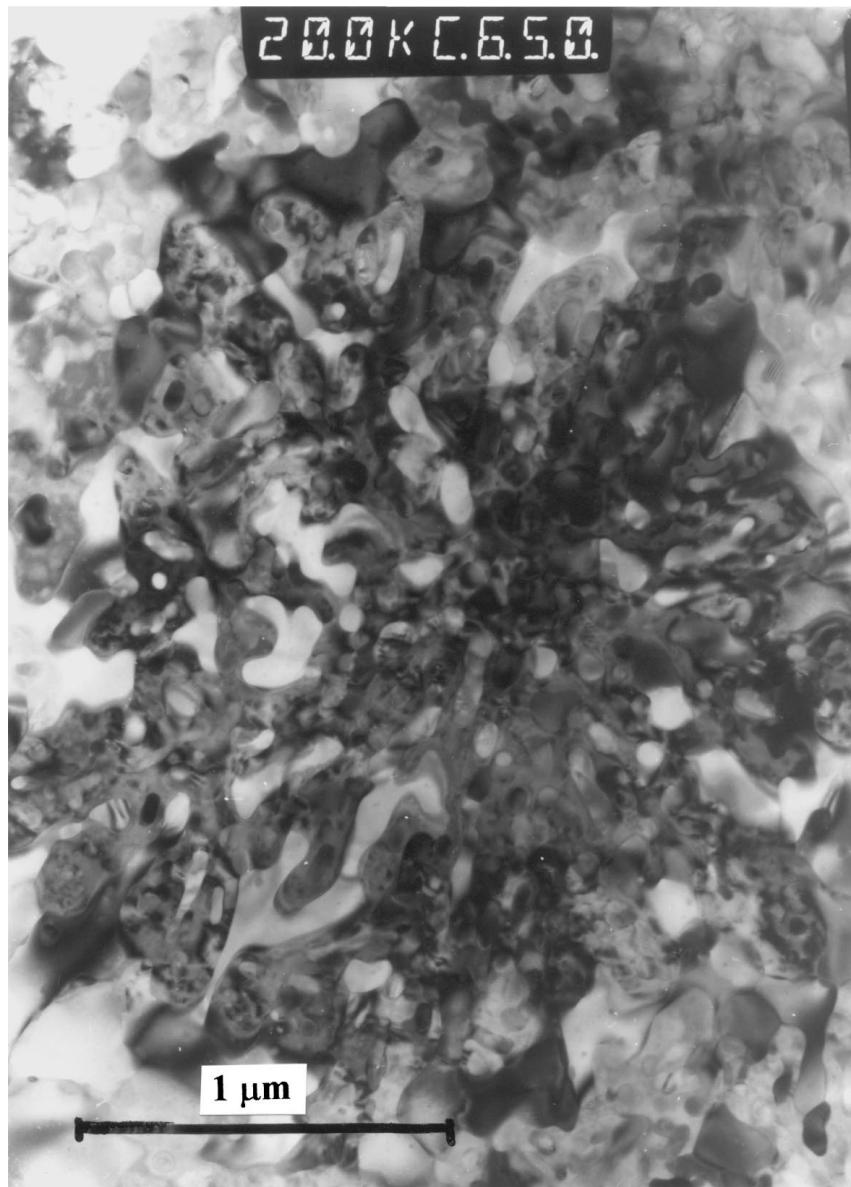


Figure 7 TEM micrograph of a sample heated to the temperature of the 3rd peak.

where F is the maximum load (50 mN) and h the residual depth of the Vickers pattern [4].

The distribution of the local Vickers microhardness is shown in Fig. 12. The curves in this figure indicate the relative frequency at which, in a series of 100 measurements on a given sample, the results fall within an interval of 25 Mpa width around H_V .

With advancing crystallization the relative frequency curve is shifted towards higher microhardness values. Besides this shift it can be observed that while the curve belonging to the as received sample is nearly symmetrical, the other curves are asymmetrical, secondary maxima or “shoulders” appear.

If the histogram taken at 900 °C is treated as the sum of two symmetrical ones belonging to the amorphous and crystalline phases then we can estimate the ratio of the amount of the HAP and the amorphous phases. According to the figure this ratio is about 58/42. It agrees well with the ratio obtained from XRD pattern.

Histograms taken at 1027 °C and 1083 °C should be superposed from three or four symmetrical histograms to obtain similar estimations for the ratio of the char-

acteristic phases. Unfortunately the uncertainty of this procedure is too high for getting an acceptable estimation.

3.3.2. Statistics of crack formation

The statistics of the crack formation was investigated on the as received sample and on those heated to the peak temperatures. The results of the measurements (cracking ratio as a function of the load) are shown in Fig. 13.

To the experimentally obtained crack probability data the $P(F) = 1 - e^{-(F/F_0)^m}$ Weibull function was fitted, where F is the load, F_0 and m are constants characterizing the crack properties of the material [6]. F_0 —the so called crack resistance force—is the load belonging to 63% crack probability. m characterizes the uncertainty of the crack formation. The lower the m , the larger the scatter of $P(F)$, i.e. the wider the transition region between the lower and higher values of the crack formation probability.

The F_0 and m values are summarized in Table I. It can be seen that with advancing crystallization the

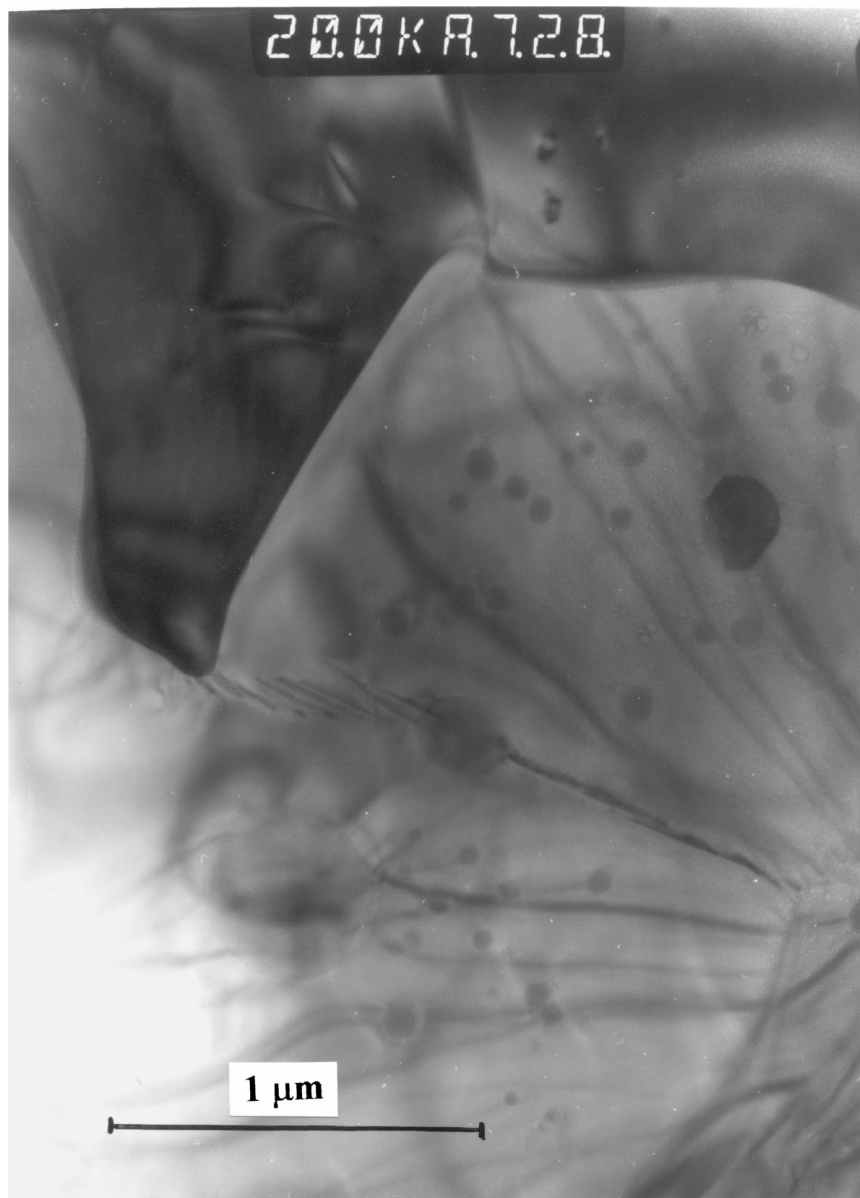


Figure 8 TEM micrograph of a sample treated at 1155 °C for 1 hour.

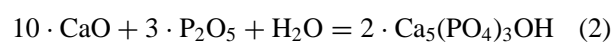
TABLE I Values of F_0 and m

Sample	F_0 [N]	m
As received	0.16	2.8
Heated to the temperature of the 1st peak	0.18	2.0
Heated to the temperature of the 2nd peak	0.21	1.9
Heated to the temperature of the 3rd peak	0.29	1.4

crack resistance force (F_0) increases monotonously. At the same time the m parameter decreases indicating increasing uncertainty in the crack formation.

4. Discussion

The electron and X-ray diffraction measurements prove that the as received material is amorphous. By heating up the sample gradually hydroxy apatite is first crystallizing by bulk nucleation. The crystallization proceeds by reaction of the components of the as received amorphous material with water, according to the stoichiometric equation:



Water is adsorbed by the surface of the constituent powders during the material preparation, CaO is produced by the decomposition of CaCO_3 due to the melting of the starting material.

Theoretically, one of the components of the starting material, CaF_2 , makes the formation of fluor apatite (besides hydroxy apatite) possible, however this compound could not be detected neither by electron nor by X-ray diffraction. It has to be noted however, that the formation of fluor apatite cannot be entirely precluded, because these two apatite phases have similar structures and consequently can be hardly distinguished by diffraction methods.

Upon heating of the as received glassy material first β -whitlockite and then wollastonite is forming. On the basis of the X-ray diffraction patterns it was found that with increasing temperature the fraction of hydroxy apatite decreases while that of β -whitlockite and wollastonite increases. In these stages of the process the fraction of the amorphous phase hardly changes (it is about 20–30%). From this it can be concluded that hydroxy apatite is partially transformed into β -whitlockite and

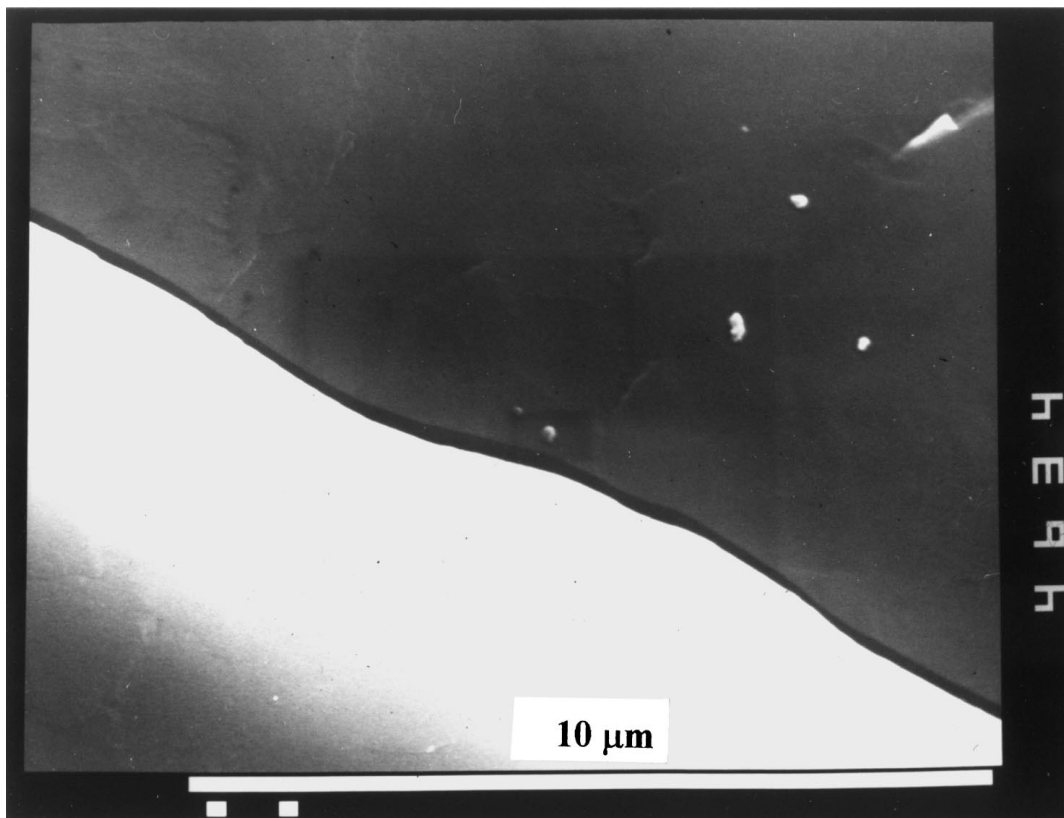


Figure 9 SEM micrograph of a sample heated to the temperature of the 1st peak.

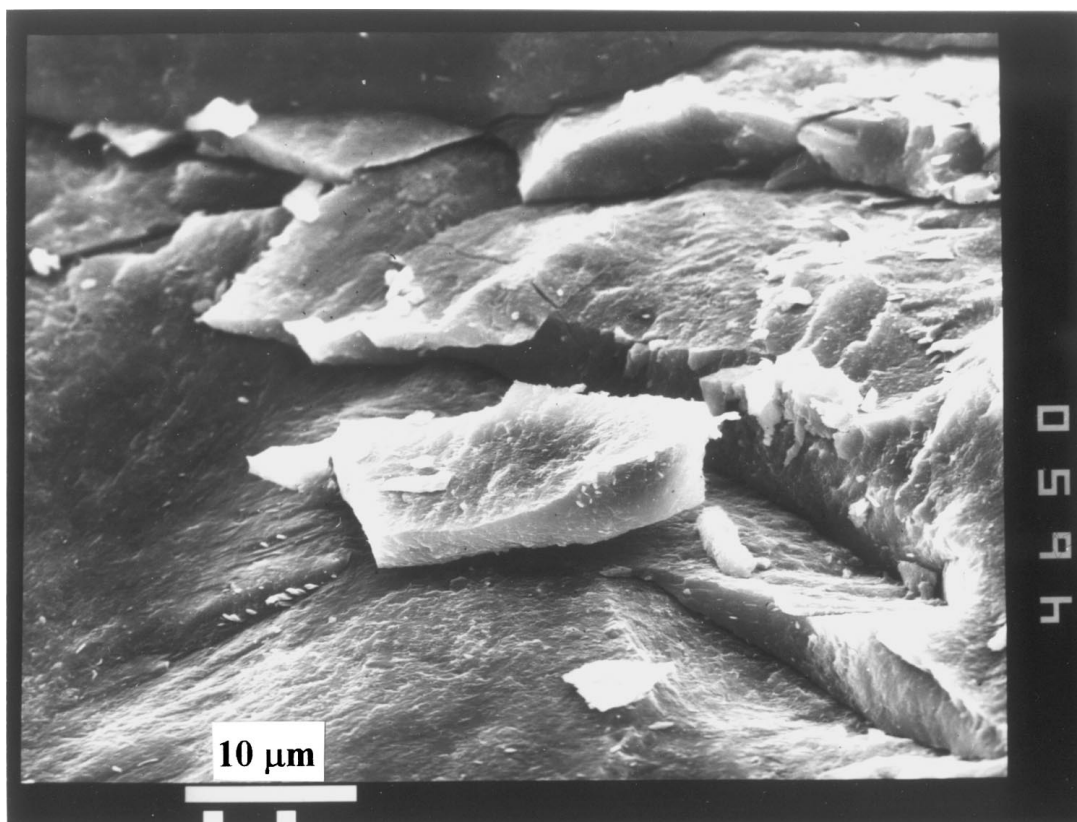


Figure 10 SEM micrograph of a sample heated to the temperature of the 3rd peak.

wollastonite. For the formation of β -whitlockite hydroxy apatite has to lose water which proceeds on the surface of the material. This explains the strong dependence of β -whitlockite formation on the specific surface of the material (see the shift of the 2nd peak in Fig. 2).

At higher temperatures hydroxy apatite is losing water and taking up silica to form wollastonite. Silica as one of the starting materials promotes the formation of the glassy phase and the network. After the first crystallization steps it remains for the most part in the

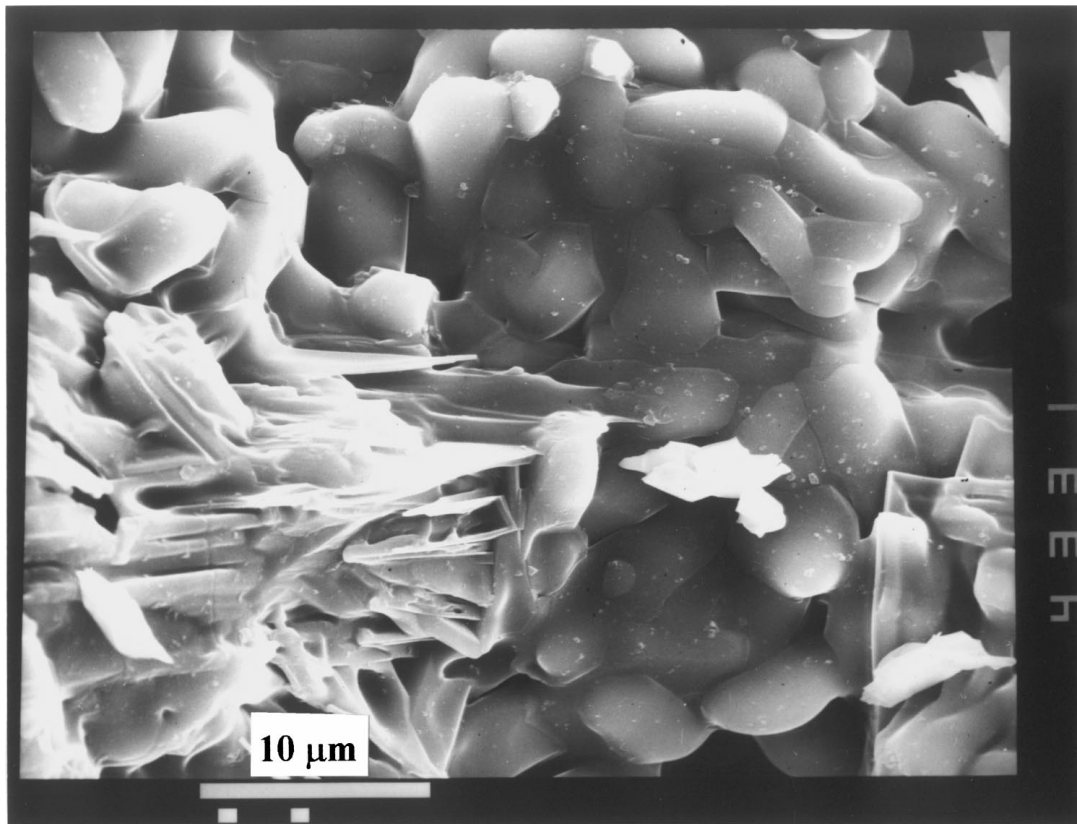
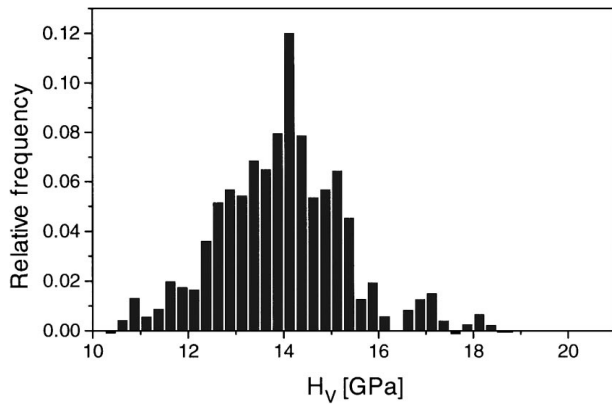
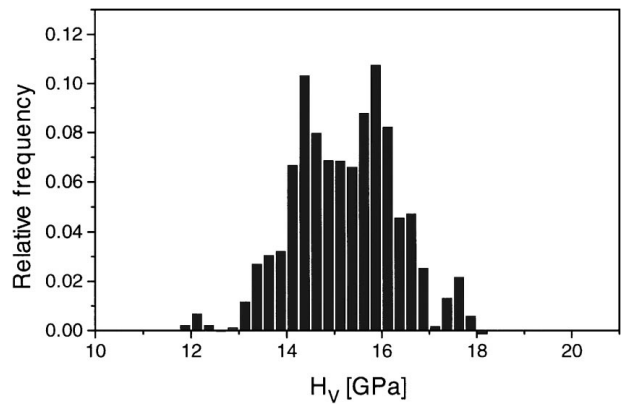


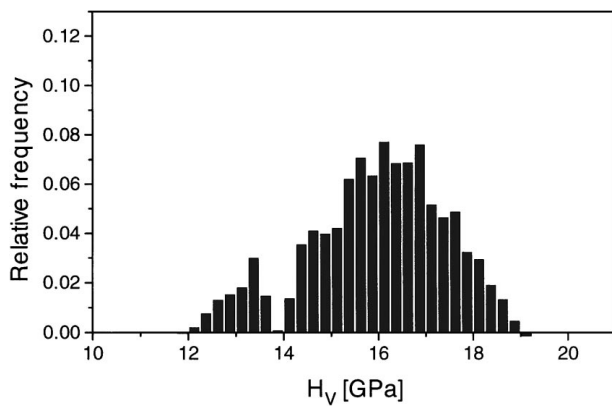
Figure 11 SEM micrograph of a sample treated at 1155 °C for 1 hour.



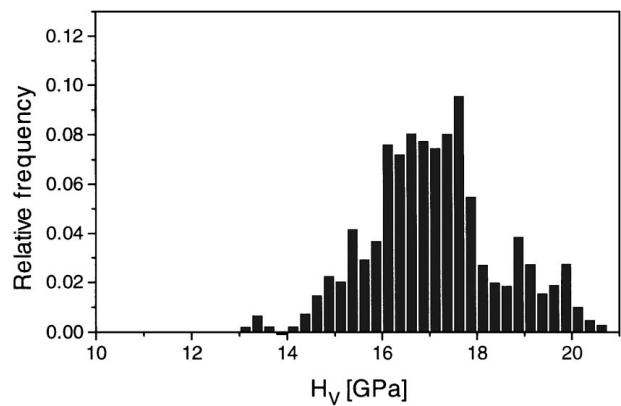
(a)



(b)



(c)



(d)

Figure 12 (a) Relative frequency diagram of the microhardness measured on the as received sample; (b) relative frequency diagram of the microhardness measured on the sample heated to the temperature of the 1st peak; (c) relative frequency diagram of the microhardness measured on the sample heated to the temperature of the 2nd peak; (d) relative frequency diagram of the microhardness measured on the sample heated to the temperature of the 3rd peak.

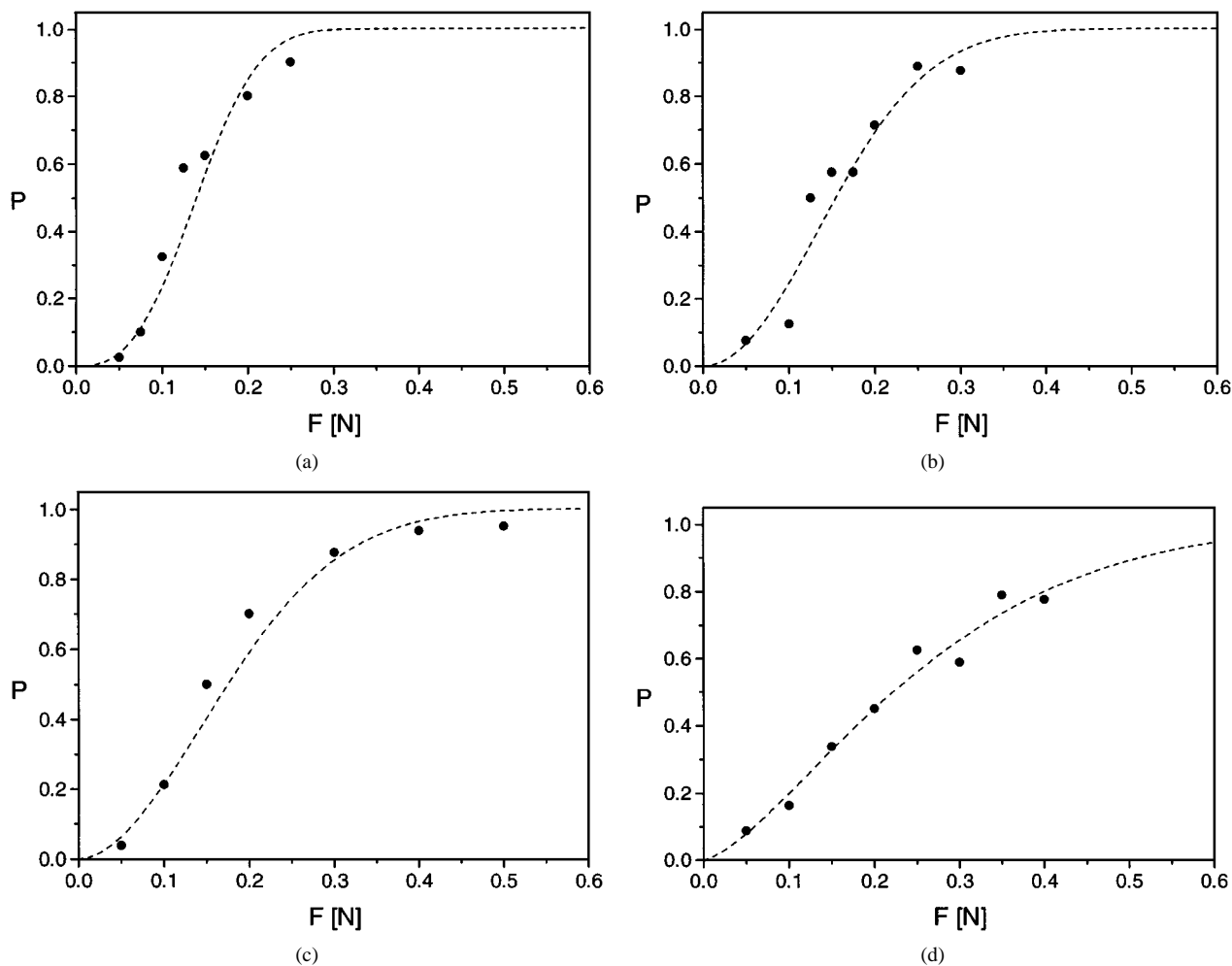
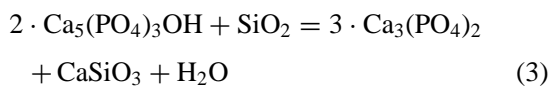


Figure 13 (a) P-F diagram obtained on the as received sample; (b) P-F diagram obtained on the sample heated to the temperature of the 1st peak; (c) P-F diagram obtained on the sample heated to the temperature of the 2nd peak; (d) P-F diagram obtained on the sample heated to the temperature of the 3rd peak.

amorphous phase filling up the spaces between the crystals. The formation of wollastonite is only possible at silica-rich sites. This explains the large fluctuations in the formation of wollastonite in the different samples. This is in agreement with the electron microscopy results according to which wollastonite could be occasionally observed on the surface of the sample heated at 1155 °C for 1 hour (see Fig. 11). The stoichiometric conditions of the formation of β -whitlockite and wollastonite are described by the equation:



The results of the mechanical investigations (microhardness distribution and crack formation statistics) can be explained on the basis of the calorimetric measurements and the microstructural investigations. The relative frequency curve of the microhardness belonging to the as received sample is nearly symmetrical, it can be approximated with the curve of a normal distribution (Fig. 12a). Its large half width indicates the chemical inhomogeneity of the glass [7–10]. With advancing crystallization both the average microhardness and the degree of the mechanical inhomogeneity are increasing. After the crystallization of hydroxy apatite the ma-

terial consists of two phases and the relative frequency curve of the microhardness has also two characteristic maxima (Fig. 12b). The first one corresponds to the average microhardness of the as received material, the second one belonging to higher values of the microhardness can be assigned to the appearance of the crystallized phase. With advancing crystallization the maximum characteristic of the glassy state becomes more and more indefinite, according to the decrease of the percentage of the amorphous phase. The second maximum is shifted towards higher values of the microhardness due to the crystallization of β -whitlockite (Fig. 12c). After the crystallization of wollastonite a definite “shoulder” appears on the side of the relative frequency curve belonging to higher values of the microhardness (Fig. 12d).

The results of the statistics of the cracks can be explained with the increasing structural inhomogeneity during the crystallization. With advancing crystallization the crack resistance force increases in accordance with the increase of the average microhardness. Simultaneously the uncertainty of crack formation at a given load increases. This uncertainty is characterized by the Weibull-modulus in the classical fracture mechanics [11]. The comparison between the crack formation statistics used in this paper and the Weibull statistics obtained on the basis of fracture testing is

described in an earlier publication [6]. The increasing uncertainty of the crack formation with heating the material to higher temperatures can be attributed to the increasing mechanical inhomogeneity. The reason for this is the development of local internal stresses as a result of the formation of different phases in the material with advancing crystallization.

5. Conclusions

The crystallization processes of a bio-active glass-ceramic material were investigated. Changes of the microstructure with advancing crystallization were observed and connected with those of the mechanical properties. It was found that:

- Hydroxy apatite, β -whitlockite and wollastonite crystallize during the heating of the material.
- The crystallization of hydroxy apatite proceeds by bulk nucleation, but that of β -whitlockite can be regarded as a surface controlled process.
- The activation energy of the crystallization of hydroxy apatite and β -whitlockite was determined.
- During the heat treatment the percentage of the amorphous phase decreases and hydroxy apatite is partially transformed into β -whitlockite and wollastonite. The structure of the material changes and the surface becomes more and more inhomogeneous.
- With advancing crystallization the average microhardness of the material increases and the crystallization results in appearance of softer and harder regions separated from each other.
- With advancing crystallization the crack resistance increases, but the uncertainty of the crack formation also increases indicating increasing mechanical inhomogeneity of the material.

It has been found that both the structural and the mechanical inhomogeneity of the material increase with crystallization.

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