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# A study on bioglass ceramics in the $Na_2O$–$CaO$–$SiO_2$–$P_2O_5$ system

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A new bioglass ceramic with composition of $Na_2O$ 12%, CaO 28%, $P_2O_5$ 10% and $SiO_2$ 50% with a high bending strength (120–140 MPa) and compressive strength (600–750 MPa) was studied. The crystallized phases of $\beta$-$Ca_2P_2P_7$ and $Na_2Ca_3Si_6O_{16}$ were determined by X-ray diffraction. Optical microscopy of the material revealed that a very uniform crystal size of about 30 $\mu$m was obtained with high nucleation frequency. The nucleation and crystallization processes were also investigated. The rat shoulder test showed that the material formed a tight chemical bond with biological texture and had good biocompatibility.

## 1. Introduction

In the early days, metallic materials were used for bone and joint replacement, however the problems of corrosion troubled researchers. After 1960, fine ceramics such as zirconia, alumina etc. were used because of their good biocompatibility and high mechanical strength. However, they do not form a tight chemical bond with bones, and they need to be mechanically locked with the bone and are liable to loosen over a long period of implantation [1, 2].

Modern medicine is served by the so-called "bioglass and bioglass ceramics" that are suitable for bone implantation in the human body and have been proved to be more biocompatible than metals and fine ceramics. It has been shown that these materials are firmly attached to bone by physicochemical forces between materials and bones. Unfortunately, their low mechanical strength makes them almost useless in clinical practice. It is especially important to achieve a high mechanical strength glass ceramic and this is favoured by a fine and uniform grained microstructure. The aim of this study is to design a glass ceramic containing small crystals which closely interlock. The production of such a microstructure fulfils the requirement for efficient nucleation, and this in turn means that careful control must be exercised over each stage of heat treatment [3, 4].

This study pointed to controlled crystallization and nucleation of the glass ceramics in the system $Na_2O$–$CaO$–$SiO_2$–$P_2O_5$ from which the material displayed a high mechanical strength and good implantation results [5].

## 2. Experimental procedure

### 2.1. Materials preparation

The specimens used in this study were based on the batch mixture of nominal composition $Na_2O$ 12%, $CaO_2$ 28%, $SiO_2$ 50% and $P_2O_5$ 10% in weight. The glass was prepared from reagent grade sodium carbonate, calcium carbonate, phosphorus pentaoxides and silica. Premixed batches were melted in a platinum crucible at 1350° C for 1.5 h and then poured on to a stainless steel plate to form a glass plate. The glass was quickly annealed at 550° C and held for 2 h to remove the residual stresses. The resulting glass plates were heated for nucleation at 730° C for 1 h and then heated to 900° C at a rate of 5° C $min^{-1}$ for crystallization and finally cooled to room temperature at 5° C $min^{-1}$. A clear view of the various stages of material preparation process is given in Fig. 1.

### 2.2. Measurement

The microstructure of the glass ceramic specimen was investigated with an optical microscope. Thin sections about 30 $\mu$m thick and about 2 cm square were prepared for optical microscopic examination. The thickness of the thin section is controlled through the microscopic observation of the interference colour given by quartz in the section.

Electron microscopic examination was performed on polished samples which has been etched with 48% HF for 20 sec. The samples examined by scanning electron microscope (SEM) were coated with a thin film of gold after etching. The nucleation condition of the glass was revealed by SEM.

The phases present in the sample were determined by powder X-ray diffraction analysis. The P-reflection of $\beta$-$Ca_2P_2O_7$ and (300) reflection of $Na_2Ca_3Si_6O_{16}$ were used to determine phase content in the glass ceramics.

Bending strength was measured by a three-point loading method using a rectangular 5 × 5 × 40 $mm^3$ specimen with 16 mm span length. The compressive strength was measured in the Kyowan 50 testing machine with a specimen of diameter of 1.3 cm and a length of 3 cm.

The rat shoulder test was used to estimate the biological compatibility of the specimen [6, 7]. Wistar rats used in the test were six weeks old and 100 g in weight at the start of the experiment. The implants were moistened with saline and placed into the rat shoulder for one month. At the end of the test period, the rat

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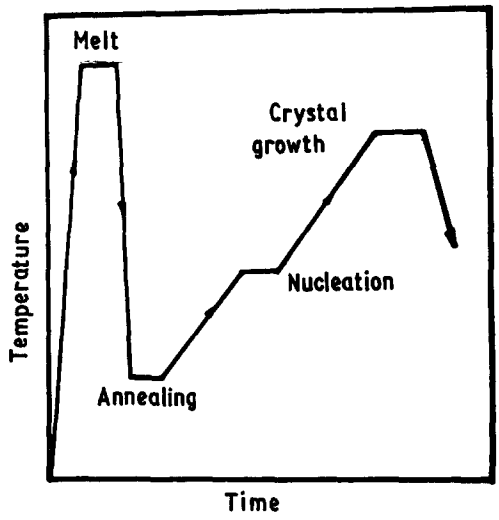


*Figure 1* The heat treatment schedule for the materials preparation.

was perfused with 10% formalin and the skin was dissected out and embedded in paraffin in contact with the implants. Sections were stained with halmatoxylin and eosin for observation.

## 3. Results and discussion

### 3.1. Nucleation

For the achievement of the desired microstructure to improve the mechanical property of the glass, it is necessary to ensure that a high density of nuclei should arise within the material. The technique for producing a fine and uniform grained glass ceramic is to generate nuclei in the glass at temperatures below those at which major crystalline phases could grow at a significant rate [5, 8]. Fig. 2 summarizes the results of such a study on the glass ceramics of weight percentage $Na_2O$ 12%, CaO 28%, $SiO_2$ 50%, $P_2O_5$ 10%, at different heat-treatment conditions. For this composition, there is a clearly defined nucleation condition of about 730° C for 50 min.

Scanning electron micrographs of the samples of maximum nucleation frequency at different temperatures are shown in Fig. 3. It is obvious that nucleation frequency initially increases with temperature up to 730° C but thereafter decreases. A general equation for the nucleation frequency proposed by

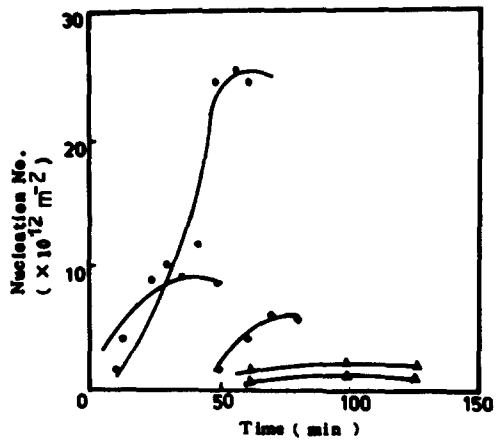


*Figure 2* Nucleation density and nucleation time at different temperatures for the glass specimen (● 750° C, ● 730° C, ◆ 720° C, △ 690° C, ▲ 670° C).

Stokes–Einstein [9, 10] gives a better approach

$$I = vN \exp\left[-\left(\Delta f_a + \frac{A}{\Delta T^2}\right)\Big/ kT\right]$$

where $I$ is the nucleation frequency and $v$ the probability that an atom makes a successful jump. As written above the exponent has two terms which do not depend upon the temperature in the same way. The first term, $\Delta f_a/kT$, represents the activation energy of the atom in the boundary jumping toward the nucleus. This term varies inversely with the absolute temperature. On the other hand, the behaviour of the second term, $A/\Delta T^2 kT$ which represents the driving force with the formation of a nucleus, is quite different. With decreasing temperature, this term falls and becomes much smaller than the first term. Since the nucleation frequency is controlled by the sum of these two terms, it has a maximum value where their sum is a minimum. In the present study, the driving forcing for the nucleation may increase at lower temperature, so that it might be expected that the nucleation will take place more rapidly. However, atomic mobility decreases very rapidly as temperature decreases, so that the sluggishness of the nucleation increases. As increasing temperature increases the atomic mobility, the driving force of the nucleation will be considerably less which may suppress the nucleation process. The net result is to have a maximum in the nucleation frequency of the glass at 730° C as observed experimentally and this is in agreement with the Stokes–Einstein equation.

From the point of view of microstructure and mechanical property, it was found that 730° C for 50 min is a better condition for this glass ceramic.

### 3.2. The role of $P_2O_5$ in the crystallization of the glass

Biocompatibility serves as the severest requirement the material must meet. Material in contact with blood should not cause thrombus formation, adverse immune response or destroy cellular tissue etc [11]. In the present study, for the sake of biocompatibility, no additives such as $V_2O_5$, $ZrO_2$ and $TiO_2$, were used as nucleation agents. It was found that the material exhibited a high nucleation density of about $2.5 \times 10^3$ N m$^{-2}$ as shown in Fig. 2. McMillan and Partridge [12] suggested that the phosphorus ion, $P^{5+}$, was in a tetrahedral condition and therefore, provided a phase separation which was due to a charge difference between the principal network-forming ions, $Si^{4+}$, and "foreign" network-forming ions, $P^{5+}$. If the phosphorus–oxygen bonds were all single bonds of the P–O type, electroneutrality could not be satisfied so that one phosphorus–oxygen bond in tetrahedral $PO_4$ would have to be a double bond. The presence of this type of double-bonded oxygen ion within the silicate network creates a condition favouring the separation of the phosphate grouping from the silicate network. In the melt, the equilibrium coordination could be compatible between the silicate and phosphate network, but phase separation will occur during reheating the quenched glass. On the basis of this investigation, it appears that the glass containing $P_2O_5$

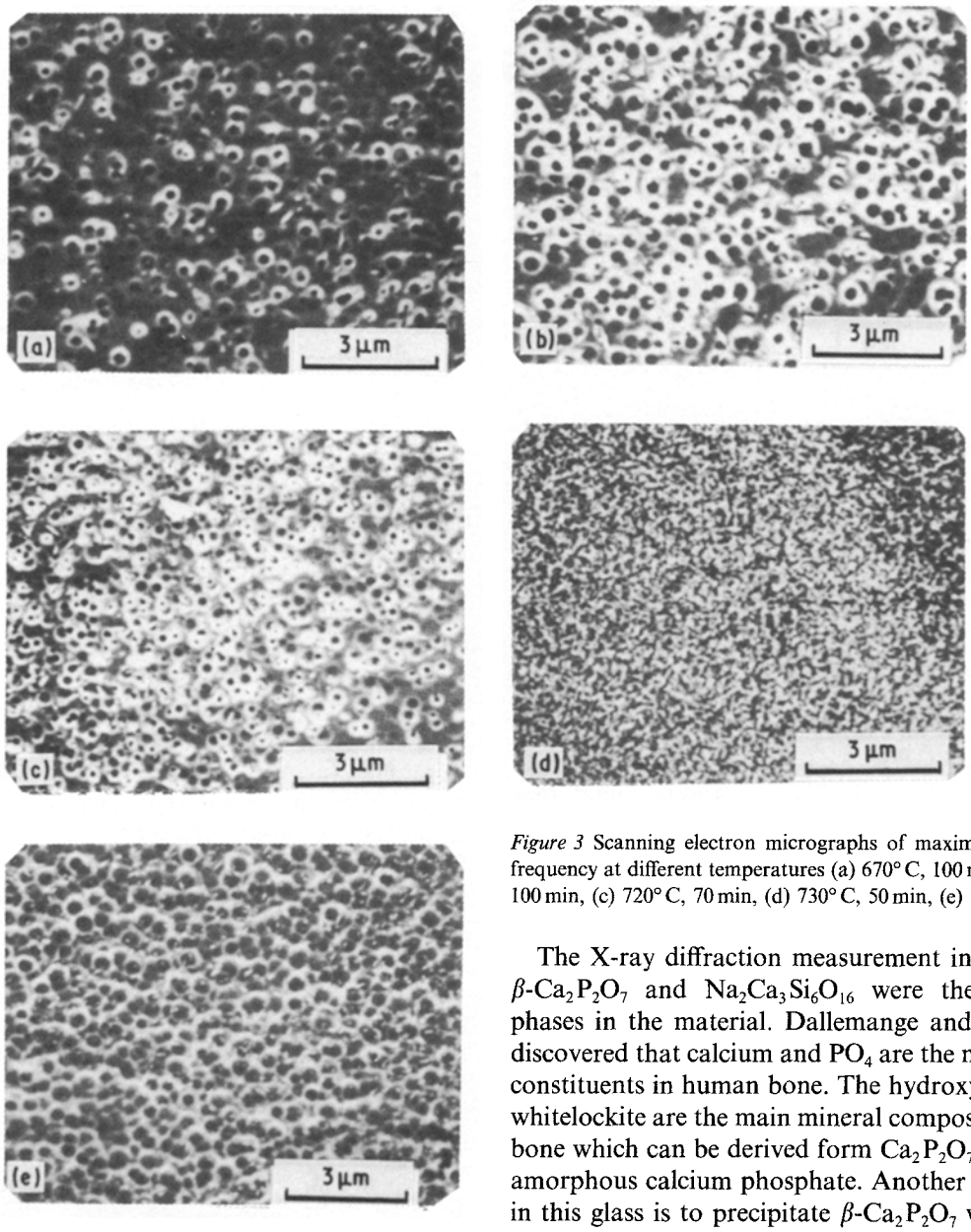


*Figure 3* Scanning electron micrographs of maximum nucleation frequency at different temperatures (a) 670° C, 100 min, (b) 690° C, 100 min, (c) 720° C, 70 min, (d) 730° C, 50 min, (e) 750° C, 30 min.

might lead to glass-in-glass phase separation as a nucleation agent in the glass. Therefore, the materials present a high nucleation density that may result in a fine and uniform grained microstructure.

The X-ray diffraction measurement indicated that $\beta$-$Ca_2P_2O_7$ and $Na_2Ca_3Si_6O_{16}$ were the crystalline phases in the material. Dallemange and Melon [13] discovered that calcium and $PO_4$ are the main organic constituents in human bone. The hydroxyapatite and whitelockite are the main mineral compositions of the bone which can be derived form $Ca_2P_2O_7$, $CaP_2O_6$ or amorphous calcium phosphate. Another role of $P_2O_5$ in this glass is to precipitate $\beta$-$Ca_2P_2O_7$ with CaO in the glass ceramics where the content of $\beta$-$Ca_2P_2O_7$ is intimate with biological texture.

The X-ray diffraction pattern of the specimen was shown in Fig. 4. The intensity of the P-peak shown in

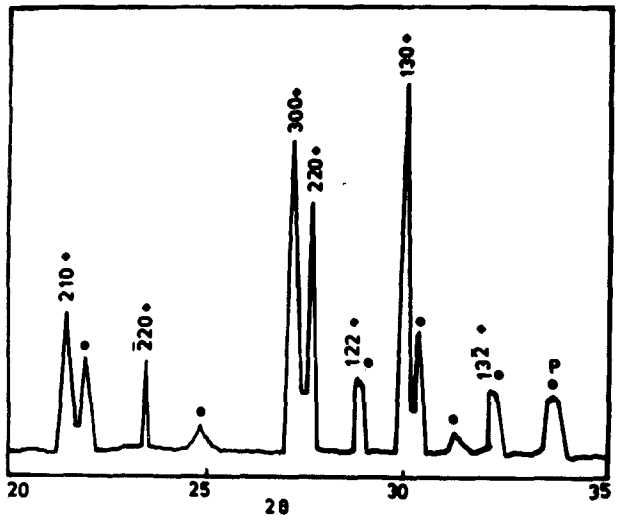


*Figure 4* The X-ray diffraction pattern of the glass ceramic after nucleation at 730° C for 50 min and then crystal growth at 900° C for 60 min. (● $Ca_2P_2O_7$, ◆ $Na_2Ca_3Si_6O_{16}$).

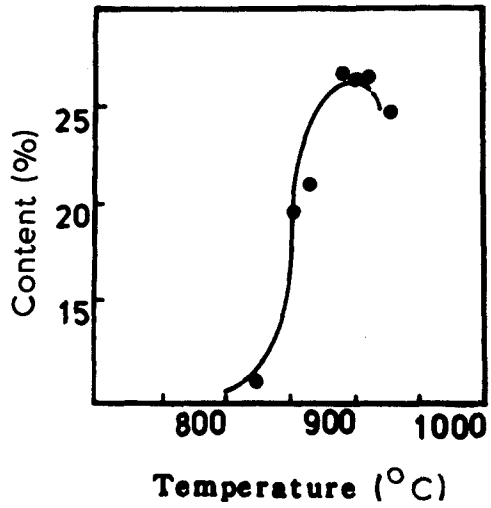


*Figure 5* Plot of content of $\beta$-$Ca_2P_2O_7$ with crystallization temperatures in the glass ceramics.

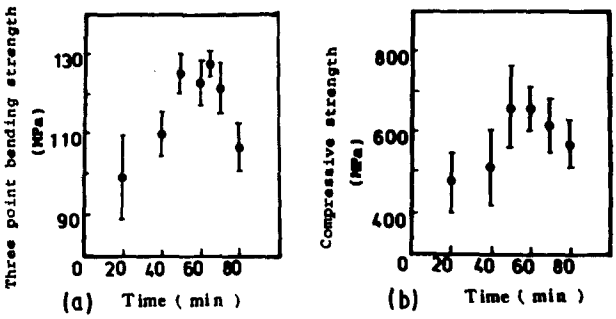


*Figure 6* Relationship between mechanical strength and crystallization time (a) three-point bending strength (b) compressive strength.

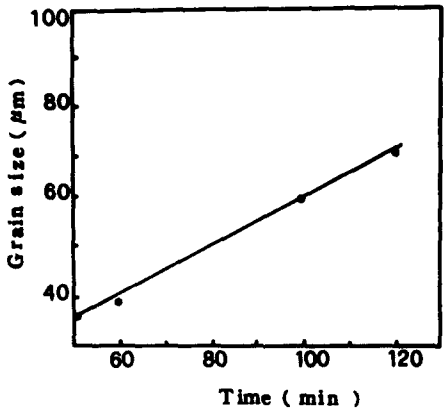


*Figure 7* The effect of crystallization time on the mean grain size in the glass ceramics.

Fig. 4 was used to determine the amount of $\beta$-$Ca_2P_2O_7$ in the glass ceramics. The content of $\beta$-$Ca_2P_2O_7$ in the material varied with crystal growth temperature as shown in Fig. 5. For the amount of $\beta$-$Ca_2P_2O_7$ under consideration, 900° C was chosen as the crystallization temperature.

### 3.3. Mechanical properties and crystallization time

The three-point bending strength and compressive strength varying with crystallization time of the glass ceramics are shown in Fig. 6. It was found that the better crystallization time of the glass at 900° C is 50–70 min as the mechanical properties were concerned. Three-point bending strength and compressive strength were 120–140 MPa and 600–750 MPa respectively. If the crystallization time of the glass is longer or shorter than that of 50–70 min, the mechanical strength is lowered. It is believed that the mechanical strength of the glass ceramics is strongly controlled by the mean grain diameter and the mean free path (which is related to the content of residual glass in the glass ceramics).

Utsumi and Sakka [14, 15] suggested that the mechanical strength of a glass ceramic is inversely proportional to the mean grain diameter and mean free path. In the present study, Figs 7 and 8 indicate that the mean grain diameter of the glass ceramics increases with crystallization time that would lead to mechanical strength decrease. The longer crystallization time decreases the content of the residual glass in the glass ceramics, therefore, decreases the mean free path and increases the mechanical strength. Thus, the mechanical strength of the glass ceramics as shown in Fig. 6 increases with the crystallization time up to 50–70 min but thereafter decreases.

After glass nucleation at 730° C for 50 min and then crystallization at 900° C for 50–70 min, the material shows an uniform grain size about 30 $\mu$m as shown in Fig. 8b.

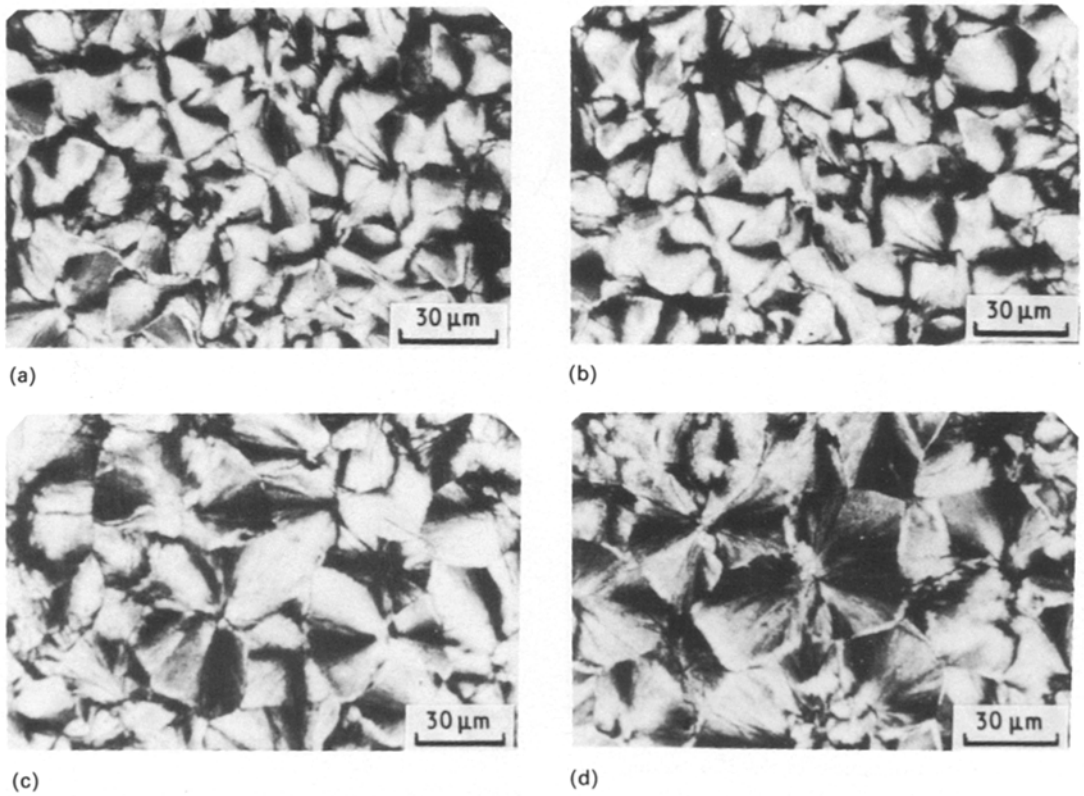


*Figure 8* Optical micrographs of the glass ceramics after crystallization (a) 50 min (b) 60 min (c) 90 min (d) 120 min.

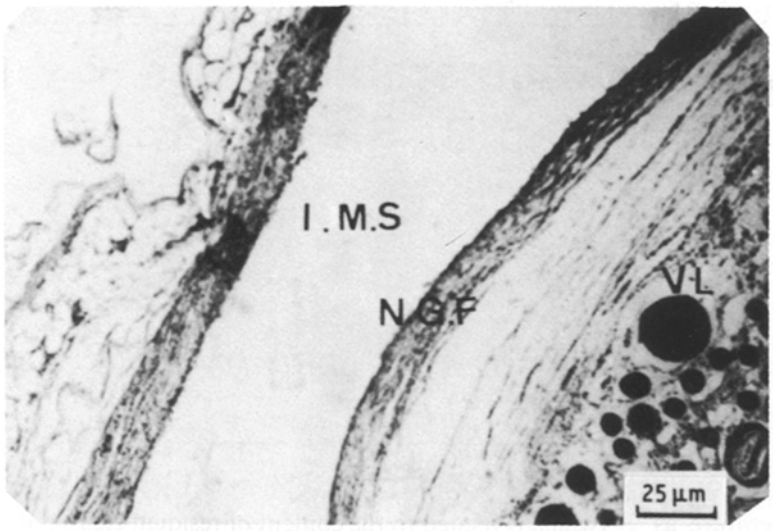


*Figure 9* Optical micrographs of rat shoulder; IMS implantation site NGF new growth fibroblast, VL vessel blood.

### 3.4. Biological test

The rat shoulder test has been recognized as a simple and rapid method for testing biomaterials experimentally. Rats recovered very soon and their skin was not allergically sensitized. No inflammation and pathological disease was observed and vessels were growing around the implanted area as shown in Fig. 9. On both epithelial surfaces adjacent to each side of the implanted area were covered with newly growing fibroblasts. The glass ceramics used in this study show a good biocompatibility when placed in intimate contact with biological texture.

## 4. Conclusions

The glass ceramic with weight percentage of $Na_2O$ 12%, CaO 28%, $SiO_2$ 50%, $P_2O_5$ 10%, showed high nucleation density of about $2.5 \times 10^3\,N\,m^{-2}$ that may be due to the glass-in-glass separation of $P_2O_5$ contained in the material. After nucleation at 730° C for 50 min, the glass ceramics exhibited a high nucleation frequency which gave the glass ceramics a fine and uniform grained microstructure. The crystallization at 900° C for 50–70 min resulted in forming a greater content of $\beta$-$Ca_2P_2O_7$ and had a better mechanical strength in the glass ceramics.

The material used in this experiment revealed no inflammation and no toxic substances were released. The implants also showed tight chemical bonding with biological tissue.

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