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Principles and phenomena of bioengineering with glass-ceramics for dental restoration

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Abstract

The main aim of this paper is to demonstrate the processes of bioengineering by controlled microstructure formation, property control and special processing. Based on the mechanisms of nucleation and crystallization, the authors deduced directions to develop of leucite-based, lithium disilicate and leucite-apatite glass-ceramics. Thus, leucite glass-ceramics were developed by surface nucleation and crystallization. Viscous flow pressing and CAD/CAM are the preferred methods of processing single units for dental restoration.

Lithium disilicate glass-ceramics were developed by heterogeneous nucleation and crystallization. The microstructure resulted in a flexural strength of approximately 400 MPa of the material. The glass-ceramic is translucent and processing by pressing of CAD/CAM in a two step process is possible. Veneered with an apatite containing glass-ceramic, the material is used as three-unit dental bridge. Fundamental research showed improvement of flexural strength.

Leucite and apatite were precipitated according to a two-fold nucleation and crystallization mechanism. The final result is a material characterized by translucency and a high C.T.E., that allows veneering of metal frameworks for dental restoration.

Keywords: Sintering; Glass ceramic; Microstructure-final; Silicate; Biomedical application

1. Introduction

Biomaterials for restorative dental applications have to fulfil fundamentally different requirements compared with those of the biomaterials used in implantology. While materials for implantological applications have to demonstrate bioactive properties, such as the ability to regenerate bone and to grow to living bone tissue, biomaterials for restorative dentistry have to simulate the characteristics of teeth or even outmatch them, as is the case with chemical durability. Restorative dental materials are mainly used to fabricate dental inlays, crowns, bridges and veneers. The most suitable materials for these applications include porcelain, glasses, sintered ceramics (Mc Lean,[1] O'Brien[2]) and glass-ceramics as well as inorganic–organic composites. Because glass-ceramics are capable of combining many different properties, these materials are widely used today.

The present paper provides a review of the most important glass-ceramics, which have been developed by the authors in the past decade. The paper focuses on the principles of glass-ceramic development and the corresponding phenomena from the point of view of bioengineering. The main aim of this review is to demonstrate the controlled development of the microstructure and the properties of these biomaterials. This process of bioengineering also involves the development of the techniques with which biomaterials are processed to make them fit for patient use. These processing techniques are predominantly used by dental technicians. However, a growing number of dentists are also applying them using CAD/CAM techniques.

The main phenomenon of bioengineering in the development of glass-ceramics is the principle of controlled crystallization of glasses (Höland and Beall[3]). As glass-ceramics are produced from base glasses, the methods for developing these materials involve controlled nucleation and crystallization. In this paper, the method of controlled surface nucleation and crystallization and that of controlled bulk nucleation and crystallization by heterogeneous nucleation will be presented. The phenomena of microstructure formation and the development of the different properties will be highlighted. A very special technique, which combines the two different methods of surface and volume crystallization will be introduced. The related application techniques will be presented for all the phenomena of nucleation and crystallization, which will be discussed.

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2. Controlled surface crystallization of leucite glass-ceramics

Sintered ceramics containing leucite have been widely used in restorative dentistry since the 1980s (Mc Lean[1]). These materials are derived from porcelains and they are produced by uncontrolled crystallization. They have been primarily used for fabricating ceramic veneering layers to mask metal frameworks.

IPS Empress® was the first glass-ceramic to be developed with a main crystal phase of leucite ($KAlSi_2O_6$). The mechanism of controlled surface crystallization was used to form crystals measuring approx 1 μm in the glass-ceramic (Höland et al.[4]). The surface crystallization processes of glasses was extensively examined by Müller et al.[5] with the conclusion that according to the classical theory of nucleation, particular importance must be attributed to the factor of elastic distortion (ΔG_E, elastic distortion enthalpy, see equation (1)):

$$\Delta G = -\frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma + \Delta G_E \tag{1}$$

where ΔG is the formation of a spherical nucleus, ΔG_V the free-enthalpy change per volume of a new phase, r the radius of nucleus, γ the interfacial enthalpy, ΔG_E is the elastic distortion enthalpy.

If the effects of elastic distortion within the process of surface nucleation in glasses are taken into account, preferred surface crystallization is clearly initiated at the points and edges of the powdered glass. In addition, the phenomena of surface and grain activation play an important role in this process. It is a well-known fact that ground glasses demonstrate a very particular surface reactivity.

The process of surface crystallization of leucite in SiO_2–Al_2O_3–K_2O glasses was closely analyzed in micrometer dimensions. Höland et al.[4] concluded that leucite, similarly to cordierite ($Mg_2Al_4Si_5O_{18}$) for example, is controlled by surface nucleation. In contrast to the formation of cordierite, leucite in its early stages grows as a flat, almost two-dimensional crystallite. A specific materials composition of 63.0 wt.% SiO_2, 17.7 Al_2O_3, 11.2 K_2O, 4.6 Na_2O, 0.6 B_2O_3, 0.4 CeO_2, 1.6 CaO, 0.7 BaO, 0.2 TiO_2 showed surface crystallization activated by a grinding process of glass granules. The nucleation and the subsequent crystallization process begins at the grain surface and advances from there into the bulk of the individual glass grains during the sintering process. Fig. 1 shows a typical leucite crystal formation in an SiO_2–Al_2O_3–K_2O–Na_2O glass. The dendritic tetragonal crystals grow from a centre like the petals of a flower.

Apart from the physical phenomena of elastic distortion and surface activation, heterogeneous crystallization processes were detected, which were initiated by seed particles (Höland et al.[4]). This heterogeneous effect was produced because the smallest glass grains crystallized and formed leucite. These microscopic crystals subsequently acted as heterogeneous nucleating agents for the initiation of nucleation in large glass grains.

A technique for producing powder compacts in the form of cylindrical ingots was developed according to the mechanism shown in Fig. 1. This technique was used to produce leucite glass-ceramics of the IPS Empress® type. The ingots were processed according to the press technique, which involves a viscous flow process, to produce dental restorations. This technique was developed on the basis of the special glass-ceramic microstructure, whose glass matrix begins to flow at approximately 10^{10} dPa s, thus allowing the material to be pressed (at 1050 or 1170 °C, depending on the type of material) into a mould. The leucite glass-ceramic, therefore, can be individually shaped to produce dental inlays, veneers and crowns. The optical characteristics and the wear resistance of the IPS Empress® glass-ceramic are similar to those of natural teeth.

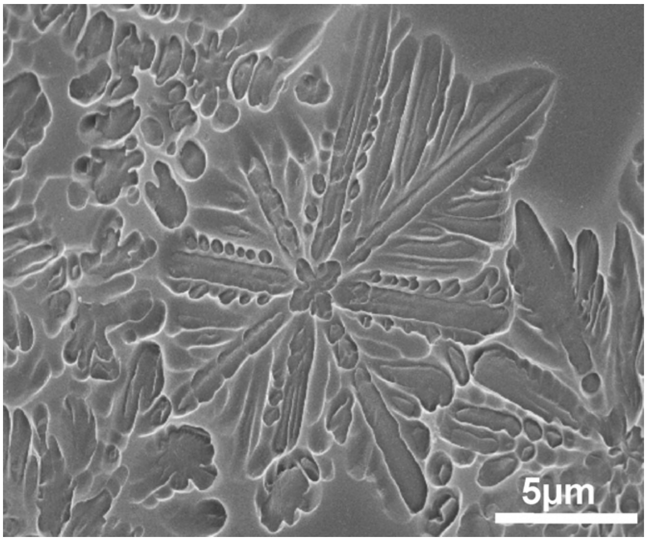

Fig. 1. Surface crystallization of leucite in an SiO_2–Al_2O_3–K_2O–Na_2O glass. Dendritic crystals grow like petals of flower. SEM, etched sample (3% HF, 10 s), Au sputtered.

Leucite-type glass-ceramic is also used as monolithic blocks to prepare dental restorations by a CAD/CAM technology. The product ProCAD® (Ivoclar Vivadent AG) is machinable, preferably applying the CEREC® system (Sirona, Germany). The glass-ceramic is characterized by translucency, a flexural strength (three point bending) of approximately 160 MPa and a fracture toughness as K_{IC} of 1.3 MPa m$^{1/2}$. Glazing the surface improves the properties of the material to a flexural strength of approximately 200 MPa. The chemical durability, according to dental standards (ISO 6872) measured a value of 36–49 μg/cm^2 after treatment with acetic acid. This allows a long term durability of the material. An adhesive cementation of the restoration is possible by applying an etching gel to produce an retentive surface and to use a special cementation material. Successful clinical tests were reported by Mörmann and Bindl.[6]

3. Controlled bulk crystallization in lithium disilicate glass-ceramics

The multi-component SiO_2–Li_2O–Al_2O_3–K_2O–ZnO materials system was closely analyzed to determine its suitability as a high-strength glass-ceramic with the objective of increasing the strength of a glass-ceramic material. This system was derived from the binary SiO_2–Li_2O system, which was well known from the development of glass-ceramics with a main crystal phase of lithium disilicate ($Li_2Si_2O_5$) (Deubener et al.,[7] Zanotto[8]). Headley and Loehman[9] discovered the mechanism of heterogeneous nucleation of lithium metasilicate (Li_2SiO_3) and lithium disilicate ($Li_2Si_2O_5$) by Li_3PO_4 through the heterogeneous nucleation and growth of Li_3PO_4 crystals by epitaxy. Headley and Loehman[9] precipitated Li_3PO_4 crystals at 1000 °C in the glass-matrix and reheated the samples to 650 and 850 °C and nucleated Li_2SiO_3 and $Li_2Si_2O_5$.

Beall[10] and Echeverría[11] developed high-strength glass-ceramics demonstrating high chemical durability in multi-component glass-ceramic systems. This development represented a significant milestone in the application of this type of glass-ceramic. Furthermore, the material showed a self-glazing effect during the manufacturing process.

3.1. Translucent, high-strength, pressable lithium disilicate glass-ceramics

During the development of high-strength glass-ceramics for restorative dental applications in the 1990s, volume crystallization of lithium disilicate was achieved in the glass powder of an extended multi-component system in the composition range of 57–80 wt.% SiO_2, 11–19 Li_2O, 0–13 K_2O, 0–5 Al_2O_3, 0–8 ZnO, 0.1–6 La_2O_3, 0.1–11P_2O_5 (Schweiger et al.[12]). This glass-ceramic had a very high crystal content with approximately 65 vol.% crystal phase of lithium disilicate (Fig. 2). The crystals measured 1–2 μm in size and formed a dense microstructure. Flexural strength of 400 MPa (measured as three-point bending) and fracture toughness as K_{IC} of 3.3 MPa m$^{1/2}$ were achieved (Höland et al.[13]). As the glass-ceramic exhibited translucent properties, it was suitable for use as a metal-free framework material for dental crowns and three-unit bridges for anterior teeth. The material was processed on the basis of the viscous flow principle like the leucite-containing glass-ceramics. However, the pressing temperature was 920 °C. Therefore, favourable prerequisites were achieved for fabricating customized artificial teeth. To improve the optical properties and achieve characteristic tooth colours in various levels of translucency, an apatite glass-ceramic was sintered onto the high-strength glass-ceramic.

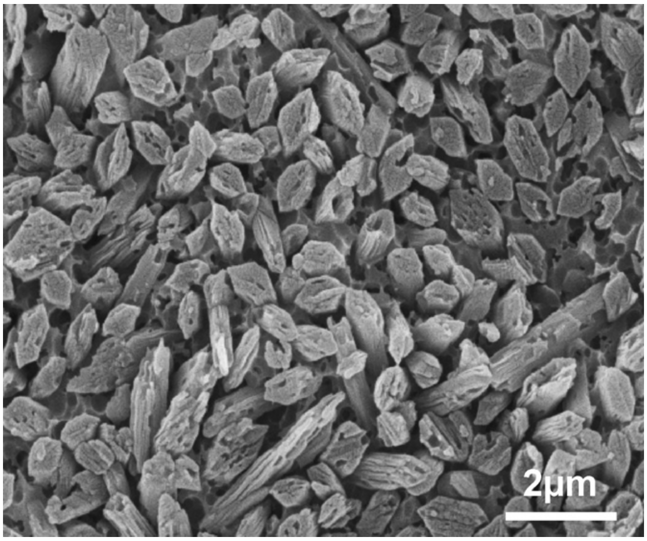

Fig. 2. Microstructure of a pressable lithium disilicate glass-ceramic (processed at 920 °C) comprising a crystal content of approximately 65 vol.%. SEM, etched sample (40% HF vapour, 30 s), Au sputtered.

The solid state chemistry and technical design principles applied in the development of this high-strength, translucent dental glass-ceramic, which is processed in a viscous state, are described below. The lithium disilicate glass-ceramic was developed into the SiO_2–Li_2O–K_2O–Al_2O_3–ZnO multi-component system by adding the heterogeneous nucleating agent P_2O_5. Instead of initiating nucleation at the surface of glass particles, the nucleating agent P_2O_5 caused nucleation throughout their entire volume. The influence of P_2O_5 on the nucleation process was dominant. Without P_2O_5, preferred surface crystallization of the glass occurred and the crystallization in the volume of the material proceeded in an uncontrolled fashion.

In an Al_2O_3-free model glass of the SiO_2–Li_2O–K_2O–ZnO base system with a composition of 63.2 mol.% SiO_2, 29.1 Li_2O, 2.9 K_2O, 3.3 ZnO and 1.5 P_2O_5 (Cramer von Clausbruch et al.[14]), high-temperature X-ray investigations showed that lithium metasilicate as well as lithium disilicate formed as primary crystal phases in dynamic heating processes at a heating rate of about 0.5 K/min at approximately 600 °C.

The suspected heterogeneous nucleating phase of Li_3PO_4 was established at temperatures above 700 °C using X-ray diffraction measurements. Nevertheless, these studies[14] have not proved that the crystalline Li_3PO_4 was the catalyst in this glass-ceramic.

3.2. High-strength, machinable glass-ceramic

In contrast to glass-ceramics, which are processed according to the viscous flow principle, materials that are machined to give them the desired shape must have fundamentally different properties. Very often, high-strength materials are very difficult to process and special equipment is required to shape them. In order to circumvent this problem, an easy-to-machine glass-ceramic, which is subsequently heat treated to achieve its high-strength characteristics, was developed. This material was produced after in-depth studies of the nucleation and crystallization processes of multi-component SiO_2–Li_2O glasses had been conducted. In an initial technological process, a lithium metasilicate glass-ceramic in the ZnO-free SiO_2–Li_2O–Al_2O_3–K_2O–P_2O_5 system with the composition of 64–73 wt.% SiO_2, 13–17 Li_2O, 0.5–5 Al_2O_3, 2–5 K_2O, 2–5 P_2O_5 was formed. In a second step, a high-strength lithium disilicate glass-ceramic was developed from this material by heat treating it (Apel et al.[15]).

In a separate study, Höland et al.[16] demonstrated results on fundamental research on nucleation, primary phase formation and solid state reactions of these type of glass-ceramic. The net result of this study was the discovery of a heterogeneous nucleation of both, Li_2SiO_3 and $Li_2Si_2O_5$ crystals by nano-scaled Li_3PO_4 phases. The surprising result of the analyzed solid state reaction characterized Li_2SiO_3 as fast growing crystals even at temperatures of 530–700 °C (Fig. 3), while $Li_2Si_2O_5$ started to grow fast at 700 °C. To explain this phenomenon, the Stokes–Einstein equation (Eq. (2)), describing the relationship

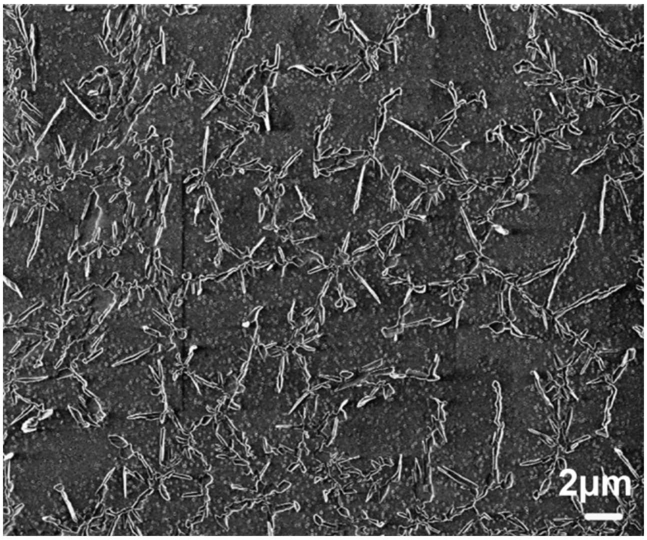

Fig. 3. Formation of Li_2SiO_3 at 560 °C/2 h in an SiO_2–Li_2O–Al_2O_3–K_2O–P_2O_5 glass. The nucleating phase (Li_3PO_4) and lithium disilicate were formed in a nanoscopic scale. High resolution SEM, etched sample (40% HF vapour, 30 s), unsputtered.

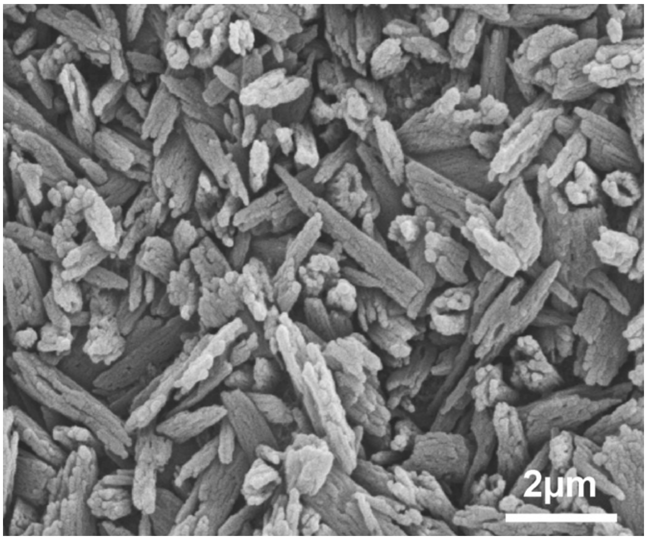

Fig. 4. Precipitation of $Li_2Si_2O_5$ at 850 °C/20 min in an SiO_2–Li_2O–Al_2O_3–K_2O–P_2O_5 glass. SEM, etched sample (40% HF vapour, 30 s), Au sputtered.

between ion mobility and viscosity, has to be considered.

$$D = \frac{RT}{r6\pi\eta N_A} \tag{2}$$

where D is the diffusion coefficient of an ion in a liquid, R the gas constant, r the radius of the ion, N_A Avogadro's number and η is the viscosity of the liquid.

The lower the viscosity (at 850 °C in comparison to 530 °C) the better the mobility of ions. Therefore, the ion transport at 850 °C results in the formation of the $Li_2Si_2O_5$ crystal phase that is close in the chemical composition of the glassy matrix. Based on this solid state reaction in the glass-ceramic the chemical equation (Eq. (3)) is valid.

$$Li_2SiO_3(\text{crystal}) + SiO_2(\text{glass}) \rightarrow Li_2Si_2O_5(\text{crystal}) \tag{3}$$

In summary, lithium disilicate and lithium disilicate were formed in nanoscopic scale, while lithium metasilicate grew to a size of 2–5 μm at approximately 560–750 °C. Due to this significant increase in the content of lithium metasilicate, a microstructure was formed, which showed very attractive machinability. This material could be used to fabricate dental restorations such as crowns and small three-unit bridges using CAD/CAM techniques. The high content of lithium metasilicate imparted the material with good processing properties as well as highly advantageous conditions for the crystallization of lithium disilicate with regard to the solid state reactions. Consequently, an interlocking microstructure of $Li_2Si_2O_5$ crystals measuring 0.5–3 μm was formed by heat treatment at 850 °C (Fig. 4). This microstructure demonstrates a higher crystal content compared with that shown in Fig. 2. Therefore, the flexural strength rose to a high value of 740.8 MPa ± 79.7 MPa (60 samples, biaxial disks), with K_{IC} of 3.3 MPa m$^{1/2}$.[16] The surface quality of this samples will be analyzed in a separate study.

4. Surface and bulk crystallization in leucite-apatite glass-ceramics

The combination of two entirely different mechanisms of nucleation and crystallization for the precipitation of two different crystal phases was achieved in glasses from the SiO_2–Al_2O_3–K_2O–Na_2O–CaO–P_2O_5–F system. A characteristic composition of 61.5 mol.% SiO_2, 9.4 Al_2O_3, 8.2 Na_2O, 7.7 K_2O, 6.0 CaO, 0.5 ZrO_2, 0.2 TiO_2, 1.9 P_2O_5, 0.5 Li_2O, 0.3 B_2O_3, 0.3 CeO_2 and 2.5 F was thoroughly examined with regard to the main phase formation of leucite ($KAlSi_2O_6$) and fluorapatite ($Ca_5(PO_4)_3F$) and the growth conditions (Müller et al.,[17] Völksch et al.,[18] Chan et al.,[19] Höland et al.[20]). All these studies clearly showed that leucite is formed according to the mechanism of surface crystallization, similarly to the description in Section 1. To take advantage of this mechanism, therefore, powdered glass was preferably used in the technological process. The nucleation of fluorapatite was initiated in the volume of the glass grains by phosphate phase separation. Although this phenomenon was undisputed, the various interpretations of the phase formation raised a number of questions. For example, the formation of a primary phase of rhenanite ($NaCaPO_4$) was clearly established, however, the subsequent reactions up to the crystallization of fluorapatite could not be fully explained.

More recent studies (van't Hoen et al.[21]) have shown that the high temperature form of rhenanite is produced after the low temperature modification of rhenanite as a result of a phase transformation. The evaluation of the HT-XRD measurements of the SiO_2–Al_2O_3–K_2O–Na_2O–CaO–P_2O_5–F glass (Fig. 5a and b), was hampered for a long time, as the clearly recorded XRD peaks looked deceptively similar to a silicophosphate phase of the $Na_2Ca_4(PO_4)_2SiO_4$ type. However, the results of the HT-XRD investigations shown in Fig. 5a and b and those of the studies conducted by Bredig,[22] Ben Almara et al.[23] and Kaprálik and Hanic[24] clearly indicate that the symmetry of the high-temperature form of rhenanite changes compared

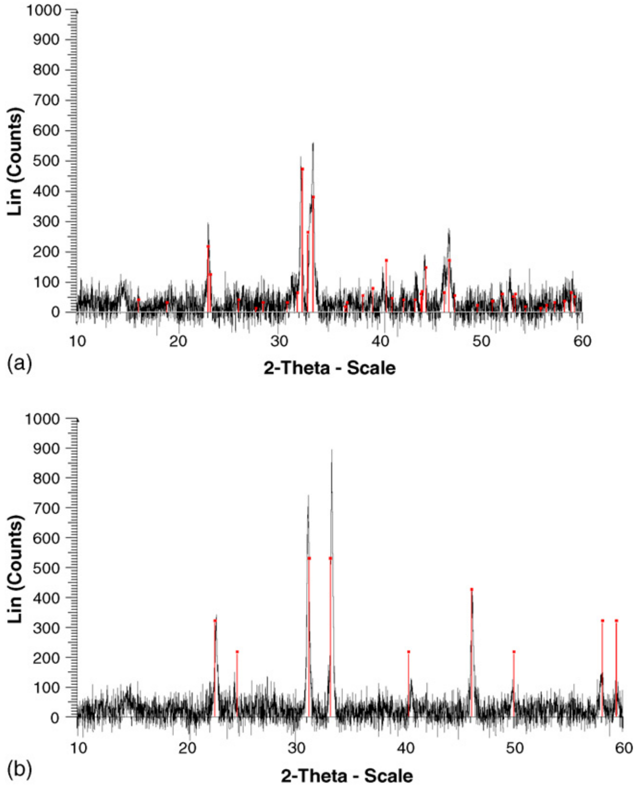

Fig. 5. High temperature XRD pattern of an SiO_2–Al_2O_3–K_2O–Na_2O–CaO–P_2O_5–F glass. (a) 600 °C: alpha $NaCaPO_4$ represents the main crystal phase acc. to ICDD-No. 00-003-0762 ($a = 0.5215$ nm, $b = 0.932$ nm, $c = 0.683$ nm/orthorhombic), (b) 640 °C: beta $NaCaPO_4$ represents the main crystal phase, acc. to ICDD-No. 00-003-0751 ($a = 0.523$ nm; $c = 0.704$ nm/hexagonal).

to the low-temperature form. Therefore, an entirely different XRD diagram resulted for the high-temperature modification of rhenanite compared with the low-temperature form. It was concluded from these results that the different phases of rhenanite represent an immediate precursor phase of fluorapatite, without the formation of an unknown intermediate phase. Fig. 6 shows the phase sequence from alpha to beta rhenanite and to fluorapatite, determined from HT-XRD up to 800 °C and of heat treated samples (900–1100 °C) analyzed by RT-XRD. Two different measurements (HT-XRD and RT-XRD) were necessary because of F-evapouration during HT-XRD measurements and a strong surface crystallization of leucite during the HT-XRD experiment.

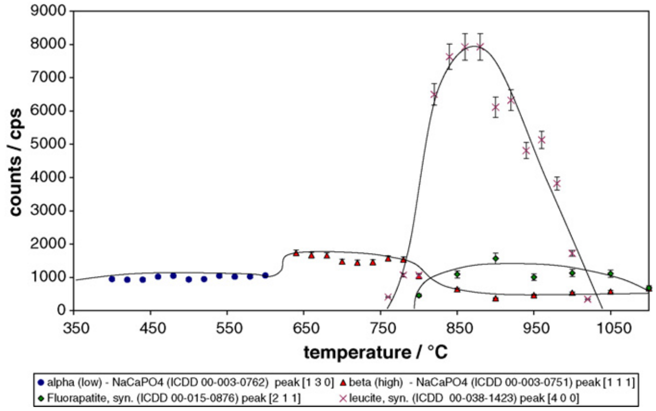

Fig. 6. Semi quantitative phase analysis in an SiO_2–Al_2O_3–K_2O–Na_2O–CaO–P_2O_5–F glass by HT-XRD (α/β-rhenanite and leucite) and room temperature XRD (apatite) of annealed samples.

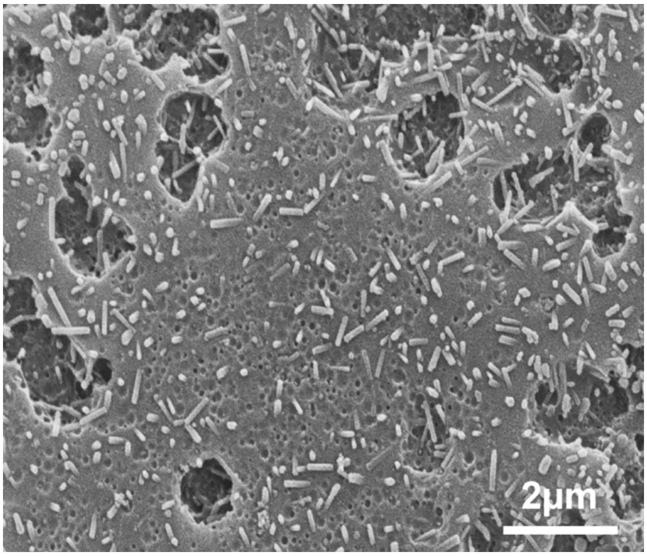

Fig. 7. Microstructure of a leucite-apatite glass-ceramic, heat treated at 900 °C/30 min. SEM etched sample (3% Hf, 10 s), Au sputtered.

The nanoscopic fluorapatite which was formed from rhenanite at 800 °C continued to grow according to the mechanism of Ostwald ripening (Müller et al.[17]), particularly at temperatures above 1000 °C. A typical microstructure, which formed in the glass grains of a powder compact, is shown in Fig. 7. Nucleation of leucite proceeds from the surface of the grain to the centre. In contrast, apatite grows with a relatively uniform crystal size of 0.5 µm and in a characteristic needle-like shape. This type of glass-ceramic, consisting of the crystal phases leucite and apatite, are applied for dental restoration to veneer metal frameworks.

5. Conclusion

We concluded the controlled microstructure formation and property development of leucite-type glass-ceramics by applying surface nucleation and crystallization mechanisms. Fundamental research demonstrated the control of heterogeneous nucleation und crystallization mechanisms to precipitate lithium metasilicate at lower temperatures of 560–750 °C and lithium disilicate at higher temperatures of 850 °C. Therefore, we concluded the development of a high strength machniable glass-ceramic.

The combination of two different nucleation mechanisms allowed the precipitation of two different phases, leucite and apatite. All materials are used in restorative dentistry.

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