J Mater Sci: Mater Med (2006) 17:1037–1042
DOI 10.1007/s10856-006-0441-y

Clinical applications of glass-ceramics in dentistry

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Received: 23 September 2005 / Accepted: 3 February 2006

Abstract Glass-ceramics featuring special properties can be used as a basis to develop biomaterials. It is generally differentiated between highly durable biomaterials for restorative dental applications and bioactive glass-ceramics for medical use, for example, bone replacements. In detail, this paper presents one biomaterial from each of these two groups of materials.

In respect to the restorative dental biomaterials, the authors give an overview of the most important glass-ceramics for clinical applications. Leucite, leucite-apatite, lithium disilicate and apatite containing glass-ceramics represent biomaterials for these applications. In detail, the authors report on nucleation and crystallization mechanisms and properties of leucite-apatite glass-ceramics. The mechanism of apatite nucleation is characterized by a heterogeneous process. Primary crystal phases of α- and β-$NaCaPO_4$ were determined.

Rhenanite glass-ceramics represent biomaterials with high surface reactivity in simulated body fluid, SBF, and exhibit reactive behaviour in tests with bone cells. Cell adhesion phenomena and cell growth were observed. Suitable colonization and proliferation and differentiation of cells as a preliminary stage in the development of a material for bone regeneration applications was established. The authors conclude that the processes of heterogeneous nucleation and crystallization are important for controlling the required reactions in both biomaterial groups.

1 Introduction

On the basis of his extensive research into the basic principles of the physical chemistry of glasses, Professor Hench opened up a promising new technology: the possibility of developing special glasses that bond directly to living bone tissue [1]. In the years following this discovery, BIOGLASS® was found to have multiple useful applications and the reaction mechanisms in biological systems were finally fully comprehended [2, 3]. Also, Professor Hench developed biomaterials for dental restorations as lithium disilicate glass-ceramics [4]. The authors of this publication would like to dedicate this article to Professor Hench in recognition of his outstanding achievements.

Glass-ceramics are used as biomaterials in two different fields: First, they are used as highly durable materials in restorative dentistry and second, they are applied as bioactive materials for the replacement of hard tissue. In this paper, an example of each of these materials will be presented. Particular attention will be paid to the subject of heterogeneous reactions. First, a brief introduction of the glass-ceramics that are used for these two different applications, i.e. as restorative or bioactive material, will be given.

The biomaterials used in restorative dentistry have to demonstrate durability in the oral environment, look like the natural tooth structure and exhibit high strength and wear resistance. In dentistry, the term 'restorative material' stands for a material that is utilized to replace the incisal and/or dentinal portion of the tooth and to reconstruct the tooth to its original shape and function. In this context, it is particularly important to maintain the vitality of the tooth. However,

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Table 1 Glass ceramics for dental restorations

Main crystal phase	Mechanism of nucleation and crystallization	Processing; application	Product name (manufacturer)
mica	internal mechanisms and phase separation	CAD/CAM; crowns, inlays	DICOR® MGC (Corning Inc, / Dentsply Int.)
leucite	surface mechanisms	pressing; crowns, inlays, veneers	IPS EMPRESS® (Ivoclar Vivadent AG)
leucite	surface mechanisms	CAD/CAM; inlays,veneers, crowns	ProCAD® (Ivoclar Vivadent AG)
leucite and fluoroapatite	surface and heterogeneous internal nucleation	sintering on metal frameworks; crowns, bridges	IPS d.SIGN® (Ivoclar Vivadent AG)
lithium zirconium silicate	internal mechanisms	pressing on posts; abutments [27]	IPS EMPRESS® Cosmo (Ivoclar Vivadent AG)
lithium disilicate	heterogeneous internal nucleation	pressing; crowns, bridges [28, 29]	IPS EMPRESS® 2 (Ivoclar Vivadent AG)
fuoroapatite	internal nucleation	sintering on lithium disilicate glass ceramic	IPS Eris® (Ivoclar Vivadent AG)
lithium metasilicate/ disilicate	heterogeneous internal nucleation	CAD/CAM; inlays, veneers, crowns, bridges	IPS e.max® CAD (Ivoclar Vivadent AG)
fluoroapatite	internal nucleation	sintering on IPS e.max® CAD	IPS e.max® Ceram (Ivoclar Vivadent AG)
fluoroapatite	internal nucleation	viscous flow on ZrO_2	IPS e.max® ZirPress (Ivoclar Vivadent AG)

non-vital teeth may also be treated with restorative materials to reconstruct or preserve the aesthetic and functional properties of the tooth. The development and processing of biomaterials has been focused on particular clinical applications, such as dental inlays, crowns, veneers, bridges and dental posts with abutments.

BIOGLASS®was used in dentistry as a bioactive material in endosseous ridge maintenance implants (ERMI) as early as in 1986. Hench [3] also used BIOGLASS® as a basis to develop bioactive glass-ceramic materials. With apatite-wollastonite glass-ceramic, Kokubo [5] developed a high strength, tough, bioactive biomaterial for orthopaedic use. Furthermore, Juhasz et al. [6] investigated composites comprising glass-ceramic components, while Kasuga and Nogami [7] developed phosphate glass-ceramics. The authors of the present study will introduce a bioactive glass-ceramic, whose main crystal phase is rhenanite, $NaCaPO_4$.

2 Clinical applications of glass-ceramics for dental restorations

As early as in the seventies, Mc Lean [8] and O'Brian [9] described the use of leucite-based sintering ceramics (crystal phase: $KAlSi_2O_6$) for the veneering of metal frameworks. These materials already provided a glimpse of the unique aesthetic properties of ceramic restorations, compared with the non-veneered metal restorations in use at the time. It is certainly safe to say that this period of time marked the beginning of the ceramic age in restorative dentistry. Replacing metal in dental applications became a particular focus of research following these developments. Dicor® was the first glass-ceramic that allowed the manufacture of inlays and crowns. The major crystalline phase present in this glass ceramic was mica [10]. Centrifugal casting technology was used for processing. Further development of this material resulted in the introduction of DICOR® MGC, a machinable glass ceramic (Table 1).

Applying the advantage of the viscous flow mechanism of glass-ceramics, leucite glass-ceramics can be processed in various shapes and, consequently, allow the manufacture of inlays and crowns [11]. This method utilizes the lost-wax technique to carry out the processing of the material. A wax pattern of the restoration (inlay, onlay, crown, veneer) is produced and then invested in a refractory die material. The wax is then burnt out to create the space to be filled by the glass-ceramic. As the glass-ceramic comprises a certain volume of glass phase, the material can be pressed into a mould using the principle of viscous flow. The translucency, colour and wear behaviour of the resulting leucite glass- ceramic restorations are adjusted to those of the natural tooth [12]. It was possible to control the crystallization process by using the mechanisms of surface nucleation and surface crystallization [13, 14]. Figure 1 shows the clinical application of leucite glass-ceramic inlays made of IPS Empress®. In addition to the pressing method, CAD/CAM procedures can also be used to manufacture leucite-based glass-ceramic

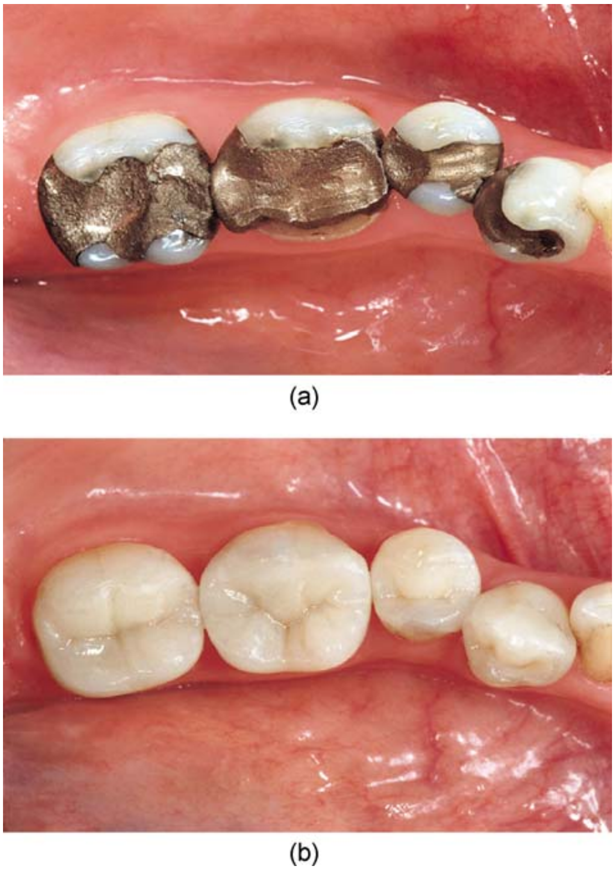

Fig. 1 Clinical application of four IPS EMPRESS® inlays/onlays. (a) preclinical situation with four amalgam fillings (b) application of leucite-type glass-ceramics (Courtesy: U. Brodbeck and Arteco Dentaltechnik, Zürich, Switzerland). (Reproduced from Höland and Beall [14] with permission of The American Ceramic Society, www.ceramics.org. Copyright 2002. All rights reserved.)

restorations (ProCAD®, Table 1). All leucite glass-ceramic restorations are bonded to the tooth structure with a luting material, preferably an adhesive bonding system. The retentive pattern produced on the glass-ceramic surface is particularly advantageous in this respect.

It was possible to develop a leucite apatite glass-ceramic (IPS d.SIGN®, Table 1) by combining two different mechanisms, i.e. controlled surface nucleation and controlled bulk nucleation. This material will be discussed in Section 3.

With the development of ZrO_2posts, a glass-ceramic that can be pressed to these ZrO_2 posts was required. In response to this need, a lithium zirconium silicate glass-ceramic was developed to adjust the coefficient of linear thermal expansion to that of ZrO_2 and to achieve a certain degree of opacity. This glass-ceramic, IPS Empress® Cosmo (Table 1), can be pressed to a ZrO_2 root canal post by using a viscous flow process. Consequently, this material provides an aesthetic solution for an abutment, to which e.g. a leucite glass-ceramic crown may be bonded in the further course of the clinical treatment.

In order to extend the range of indications of glass-ceramics from inlay and crowns to three-unit bridges, a biomaterial that offers high strength, high fracture toughness and, at the same time, a high degree of translucency was required. The result of this development was a lithium disilicate glass-ceramic (IPS Empress® 2, Table 1). With a flexural strength of approx. 400 MPa and a K_{IC}value of 3.3 MPa · m $^{1/2}$, both the flexural strength and fracture toughness of lithium disilicate glass-ceramic are almost three times of those of leucite glass-ceramic. Lithium disilicate glass-ceramic ingots are utilizied to produce the crown or bridge framework in combination with the pressing technique, i.e. the viscous flow process. To further improve the aesthetic properties, i.e. translucency and shade match, and to optimally adjust the wear behaviour to that of the natural tooth, the lithium disilicate glass ceramic is veneered with an apatite-containing glass-ceramic using a sintering process. Figure 2 shows a clinical application of this glass-ceramic system, in this case a three-unit bridge.

In order to meet the demanding requirements of CAD/CAM applications, a lithium metasilicate glass-ceramic, IPS e.max® (Table 1) was developed [15]. This material, which is supplied in a typically blue colour, has been especially designed for the milling process in the CAD/CAM technique. After the milling process, the material is subjected to thermal treatment, which results in a lithium disilicate glass-ceramic that demonstrates a characteristic tooth colour. The resulting dental restorations can be polished and completed with glazing and characterization materials.

The range of IPS e.max® products also encompasses various apatite-containing glass ceramics that are suitable for both layering material on lithium disilicate glass-ceramic and veneering material on ZrO_2 sintered ceramic. The apatite crystal phase of the $Ca_5(PO_4)_3F$ type acts as a component that adjusts the optical properties of the restoration to natural tooth. For this reason, the crystallites are of nanoscale dimension.

Fig. 2 Three-unit dental bridge consisting of a lithium disilicate framework (IPS EMPRESS® 2) veneered with fluoroapatite containing glass ceramic (IPS ERIS®)

Table 2 Fabrication of glass-ceramic units per end of 2004

Type of glass ceramic	Number of units
IPS Empress®	27 000 000 (1991–2004) (14 years of clinical experience: more than 90% success rate)
IPS ProCAD®	3 200 000 (1998–2004)
IPS d.SIGN®	55 000 000 (1998–2004)

Table 2 provides an overview of the frequency of use of different glass-ceramics for dental restorations. This evaluation was performed on the basis of estimated numbers of units of dental restorations produced worldwide. A unit is, for instance, an inlay or a crown; the bridge of Fig. 2 counts three units. If the materials are ranked according to their frequency of use, it becomes apparent that veneering materials for metal frameworks (IPS d.SIGN®) continue to be the most frequently used glass-ceramic materials, having been used in 55 000 000 units (7 years). Furthermore, metal-free systems have also revealed a high frequency of use, with IPS Empress®having been used in 27 000 000 units (14 years).

3 Leucite-apatite glass-ceramic, a restorative biomaterial

The leucite-apatite containing glass-ceramic is derived from the SiO_2-Al_2O_3-Na_2O-K_2O-CaO-P_2O_5-F system. A special type of this group has the following composition in wt%: 54.6 SiO_2, 14.2 Al_2O_3, 8.4 Na_2O, 10.7 K_2O, 5.0 CaO, 0.9 ZrO_2, 0.2 TiO_2, 4.0 P_2O_5, 0.2 Li_2O, 0.3 B_2O_3, 0.8 CeO_2 and 0.7 F [14]. The glass-ceramic was prepared according to the classic method of glass-ceramic formation: melting, casting to prepare a glass frit, controlled nucleation and crystallization. A two-fold reaction mechanism leads to the precipitation of fluoroapatite, $Ca_5(PO_4)_3F$ and leucite, $KAlSi_2O_6$ [14]. Leucite was grown by surface nucleation and crystallization mechanism from the surface of the grains at 700–1050°C and fluoroapatite according to bulk nucleation and crystallization at 800–1050°C. However, prior to leucite and fluoroapatite formation, a precursor phase of rhenanite, $NaCaPO_4$, was analysed by X-ray diffraction. In the formation of $NaCaPO_4$ the low temperature modification (α-phase) is precipitated first. The high temperature form (β-phase) is transformed from the α-phase at temperatures above 640°C [16]. The crystal parameters of β-rhenanite are: $a = 0.523$ nm, $c = 0.704$ nm of the hexagonal system [17]. Fluoroapatite is characterized as a hexagonal phase with $a = 0.9367$ nm, $c = 0.6884$ nm [18]. The lattice parameter c of both crystals are very similar. Another similarity is also given with the a-axis lattice parameter of β-rhenanite ($a = 0.523$ nm) by doubling ($2\,a = 1.046$ nm). This value is close to that of fluoroapatite. Based on these structural similarities of both crystals and their thermal stability at high temperatures, the modification of β-rhenanite may promote the nucleation of fluoroapatite.

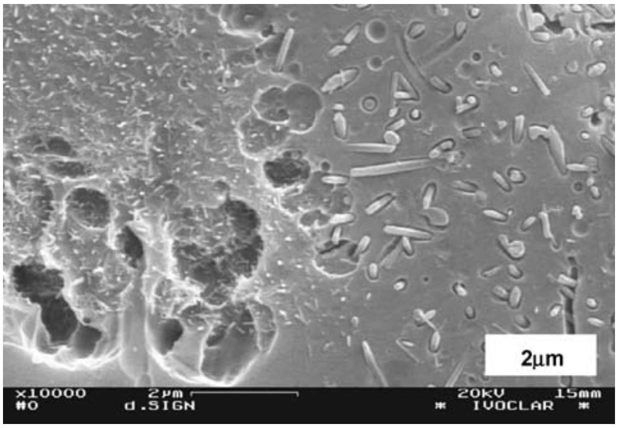

Fig. 3 Microstructure of a glass ceramic with leucite and needlelike flouroapatite crystals. SEM after etching (3% HF, 10 sec.). (Reproduced from Höland and Beall [6] with permission of The American Ceramic Society, www.ceramics.org. Copyright 2002. All rights reserved.)

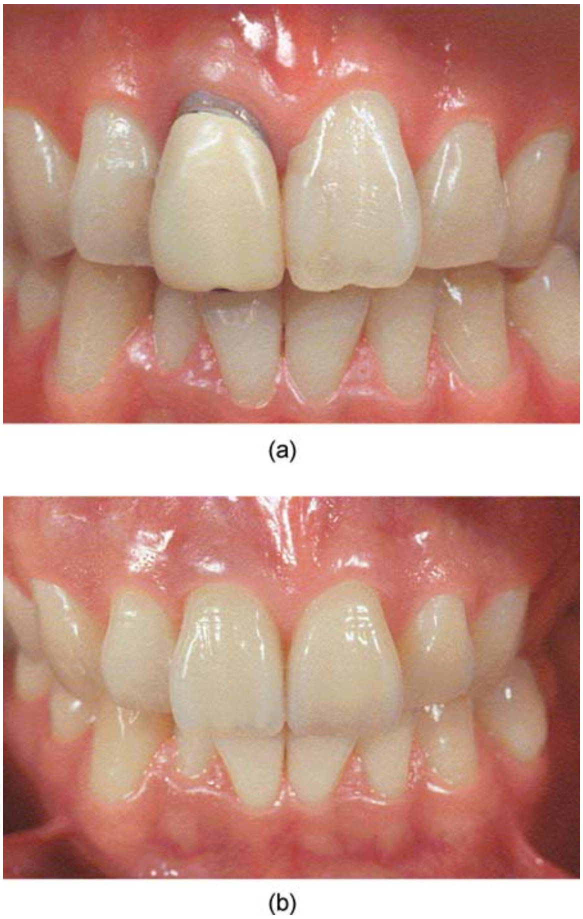

Fig. 4 Clinical application of leucite-fluoroapatite glass-ceramic (IPS d.SIGN®). The glass ceramic was veneered on a metal framework of a dental crown (tooth 11). (Courtesy: S. Kataoka, Japan) (a) preclinical situation (b) application of leucite-fluoroapatite glass-ceramic

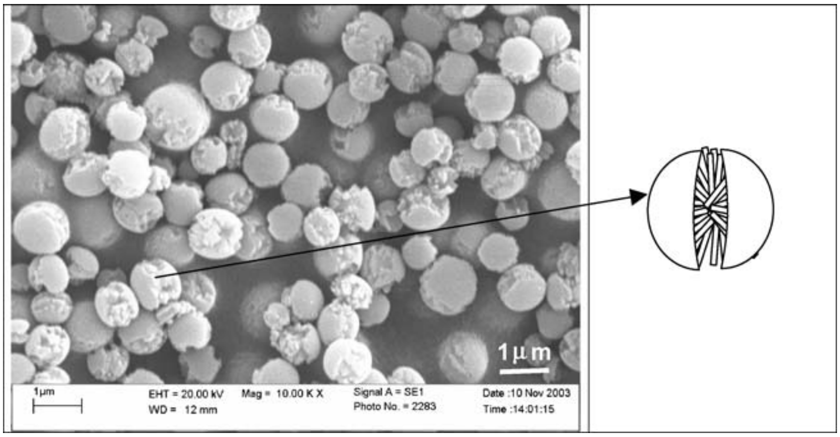

Fig. 5 Formation of a calcium phosphate crystal layer on rhenanite glass-ceramic (containing approx. 6 wt% P_2O_5) after immersion in C-SBF for 10 days. SEM

The crystal growth of fluoroapatite follows an Oswald ripening mechanism [14]. The SEM in Fig. 3 shows the two-phase crystal content of apatite and leucite in a sample heat treated at 1050°C. The needle-shaped crystals represent the fluoroapatite phase and the deeply etched oval areas the leucite crystals. With the chosen HF-etch preparation method, the SiO_2-rich areas are selectively etched, while the phosphate is left untouched. The clinical application of this glass-ceramic has been proven to be suitable for clinical application as veneering material on metal frameworks for single units (Fig. 4) as well as for large dental bridges involving more than three units.

4 Rhenanite glass-ceramic, a bioactive biomaterial

Based on the function of rhenanite as precursor phase of fluoroapatite, glass-ceramics containing rhenanite as main crystal phase have been developed [19, 20]. Rhenanite is also known as weak interface to hydroxyapatite [21, 22]. The similarity of crystal parameters of hydroxyapatite and rhenanite is obvious as shown for fluoroapatite and rhenanite in section three.

In this paper, the surface properties of a glass-ceramic with 58 wt% SiO_2, 6 P_2O_5 , 22.8 Na_2O, 12.9 CaO and 0.3 F are presented. The base glass of this glass-ceramic was annealed at 900°C for 1 h and isolated rhenanite crystals of a diameter of approx. 300 nm were precipitated in the glassy matrix. The conventional SBF (C-SBF) was used to test the reactivity of glass-ceramics and cell culture examinations were carried out to study the biological reactions.

The reactivity of the rhenanite glass-ceramic in C-SBF is characterized by a multi-phase process, which proceeds similarly with BIOGLASS® [2] and other bioactive glass- ceramics [5]. The special effect that characterizes the formation of hydroxyapatite-type crystal growth is their heterogeneous, catalytic effect induced by rhenanite crystals [23]. Crystals grow at first as hemispheres and finally form spherical crystals (Fig. 5). Busch et al. [24] observed a similar phenomenon in amorphous gels, but those fluoroapatite crystals grew much lager in size.

The interaction of rhenanite glass-ceramics on human osteoblastic SAOS-cell proliferation, alkaline phosphatase (ALP) activity and typ-1 collagen synthesis was examined. In the current experiments, human osteoblastic SAOS-2 cells were adhered to the bioactive glass- ceramics and showed at all times of cultivation a characteristic morphology (Fig. 6). Processing a high cell proliferation capacity, the cells reached confluence and formed a multilayer by day 14. At the same time, an ALP activity of 0.32 units per 10^6 cells was examined, which was increased in comparison to culture flasks (70 fold). After differentiation of the osteoblastic cells and matrix maturation was initiated, a further increase in the number of cells was observed, while some cells detached during the last three weeks of *in vitro* cultivation. Most interestingly, increased ALP activity and collagen synthesis

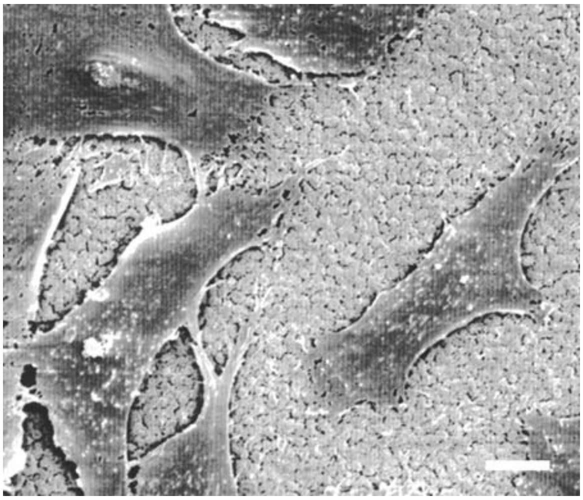

Fig. 6 Morphology of human osteoblastic SAOS-2 cells attached to rhenanite glass-ceramic analyzed by SEM two days after seeding. The glass-ceramic was immersed in simulated body fluid (SBF) for 10 days and afterwards incubated in the medium for 3 days (bar = 10 μm)

(matrix protein) were observed, which was also shown by Hatter et al. [25]. The time-dependent decrease of ALP activity can also be ascribed to the increasing differentiation of the cells into osteoblastic cells, characterized by matrix maturation and mineralization [26]. The present results revealed that rhenanite glass-ceramic causes stimulation of osteoblastic differentiation in a biomimetic way. It can therefore be concluded that this material has potential for being used in clinical applications.

5 Conclusion

We conclude that heterogeneous nucleation processes assume an important function in the process of crystal formation in both, the bulk of glass-ceramics for dental restoration and on the surface of bioactive biomaterials. First, the crystals of fluoroapatite were precipitated by a heterogeneous reaction in glass- ceramics for dental restorations. Second, the surface reaction of the bioactive rhenanite glass-ceramic is also induced by a heterogeneous process. The rhenanite crystal of the glass-ceramic catalyze the formation of hydroxyapatite-type crystals.

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