Sintered glass-ceramics for dental applications

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Abstract

Sintered glass-ceramics are very important to the development of biomaterials for restorative dentistry. The following systems have shown to be particularly suitable: SiO_2-Al_2O_3-K_2O (leucite), SiO_2-Al_2O_3-K_2O-CaO-P_2O_5-F (leucite, apatite), SiO_2-Al_2O_3-CaO-P_2O_5-F (apatite), Li_2O-SiO_2 (lithium disilicate) and SiO_2-P_2O_5-Li_2O-ZrO_2 (ZrO_2 crystals). The principles involved in developing materials of this kind and the applications of these materials will be shown in the following survey.

1. Introduction

Biomaterials in sintered form play an important role in restorative dentistry. These materials are predominantly used to mask metals in the form of crowns, veneers or inlays. They are not bioactive, however, they are characterized by particular optical, mechanical, thermal and chemical properties. The objective in developing these materials is to simulate the characteristics of natural teeth as closely as possible.

The first veneering materials for metal frameworks used in dentistry were mentioned by McLean /1/. The materials used at that time were derived from porcelain systems. In the early 1990s, glass-ceramics that contained a main crystal phase of leucite ($KAlSi_2O_6$) were developed. In the process, it was shown that with a suitably high leucite content strength values could be achieved that would enable glass-ceramics to be used without a metal substrate.
In this report, we will discuss the different stages of the development of the different types of sintered glass-ceramics with reference to the published literature. A corresponding monograph /2/ of all the practically used sintered glass-ceramic systems is available. This report will begin by addressing the leucite system.

Two fundamentally different nucleation and crystallization mechanisms were used to develop glass-ceramics, specifically, volume and surface crystallization. The different mechanisms will be discussed in the following sections.

2. Glass-ceramics systems as sintered materials

2.1. The leucite system

In the SiO_2-Al_2O_3-K_2O system it is possible to produce glass-ceramics with a main crystal phase of leucite ($KAlSi_2O_6$) by controlled surface crystallization. The mechanism of surface crystallization proceeds in a fashion similar to that observed in cordierite glass-ceramics /3/. A typical composition is in the range of 59 to 63 wt% SiO_2, 19-23.5 Al_2O_3, 10-14 K_2O, 3.5-6.5 Na_2O and additives. It is interesting to note that similar to cordierite crystallization, an intermediate phase with a highly disordered structure develops after nucleation in the formation of leucite. After the formation of this intermediate phase at approximately 700 °C, leucite forms as the temperature is increased above 700 °C. It develops directly at the surface of monolithic samples and grows into the volume of the glass.

In fundamental studies, surface crystallization is usually examined using monolithic samples. This method, however, has not produced successful results for practical applications. To this end, granules or fine powders have to be produced to ensure the successful fabrication of products made of sintered glass-ceramics. Surface crystallization then occurs at the grain boundaries, forming what is sometimes called a "ghost inner surface". Glass-ceramics produced according to this mechanism exhibit fracture toughness exceeding 100 MPa. Consequently, these materials can be used on metal substrates or in self-supporting form.

Surface crystallization can also be combined with phase separation processes in the volume of the glass. The following composition range is typical: 48 to 66 wt% SiO_2, 5-20 Al_2O_3, 3-15 K_2O, 3-12 Me(II)O (with Me= Ca, Mg, Sr, Ba), 0.5-5 P_2O_5 and additives /4/. These mechanisms were successfully combined to produce opalescent glass-ceramics, which can mimick the appearance of natural teeth.

2.2 Leucite-apatite glass-ceramics

Simultaneous control of surface and volume crystallization processes led to the formation of leucite-apatite glass-ceramics. Compared with the classical leucite system, this material has been developed into a comprehensive multi-component system. The following composition range is typical: 49 to 58 wt% SiO_2, 11-21 Al_2O_3, 9-23 K_2O, 1-10 Na_2O, 2-12 CaO, 0.5-6 P_2O_5, 0.5-2.5 F and additives /5/. Leucite

forms according to a surface crystallization mechanism, as in the basic leucite system. In contrast, however, apatite is formed according to the mechanism of volume crystallization. Nucleation, which is decisive for the development of the phase is controlled through phase separation processes. A drop-shaped CaO-P_2O_5-rich glass phase forms the starting point from which $NaCaPO_4$ precipitates as the primary crystal phase. By way of several additional intermediate phases, apatite then forms. This complex mechanism has already been mentioned /2/. It is interesting to note that apatite develops in its well-known hexagonal morphology at temperatures below 1000 °C and in needle-like form above 1000°C.

Thus, if glass grains of the above composition are used, two entirely different crystal phases can be produced in one material through controlled nucleation and crystallization. Dental products produced in this way demonstrate special optical properties and favourable wear characteristics in relation to natural teeth. The material in powdered form is used to fabricate veneers for metal substrates (eg crowns and multi-unit bridges).

2.3 The lithium disilicate system

Lithium disilicate glass-ceramics, which were developed by Stookey, were the first glass-ceramics ever to be produced /2/. Comprehensive studies based on this fundamental material took place in various directions. The starting point of all these studies was the basic binary materials system. The most significant advances in relation to their practical application have been achieved by Beall /6/. The chemical durability of these materials has been considerably improved compared with previous systems. The sintered glass-ceramics presented in this paper are derived from the following composition range: 57 to 80 wt% SiO_2, 0 – 5 Al_2O_3, 0.1 –6 La_2O_3, 0-5 MgO, 0-8 ZnO, 0-13 K_2O, 11-19 Li_2O, up to 11 P_2O_5. Volume nucleation is achieved by adding P_2O_5. Depending on the composition range, the phase sequence for the formation of the main crystal phase lithium disilicate ($Li_2Si_2O_5$), however, is different and has to be controlled by specific mechanisms /2, 7, 8/.

Controlled volume nucleation and crystallization was used to fabricate a very strong and tough lithium disilicate glass-ceramic for metal-free biomaterial systems. The application of this material together with a sintered glass-ceramic will be discussed in the next section.

2.4 Apatite glass-ceramics

Apatite glass-ceramics can also be produced without additional crystal phases. In the following example, the objective of producing a low crystal concentration to develop special optical properties was pursued. Needle-like fluorapatite crystals ($Ca_5(PO_4)_3F$) were formed in the composition range of 56 go 65 wt% SiO_2, 1.8-5.3 % Li_2O, 9-17.5 % K_2O, 9-16 % ZnO, 3.5-10.5 % CaO, 2-6 % P_2O_5, 0.5 – 1.0 % F /9/. Crystalline glass nano-microstructures were produced as an intermediate stage. In contrast to phase formation in the leucite-apatite system, no crystalline transitional phases develop prior to the formation of apatite.

The apatite glass-ceramic is ideal for applying veneers to the lithium disicilate glass-ceramics mentioned in section 4. The veneer is applied by sintering the apatite glass-ceramic onto the other material. Since apatite crystals have a needle-like shape, similar to the apatite crystals of the natural tooth, natural optical properties are achieved. This glass-ceramic system made of lithium disilicate and apatite glass-ceramics is successfully used as a metal-free crown and bridge material (three-unit bridges) in dentistry. This application is shown in Fig 1.

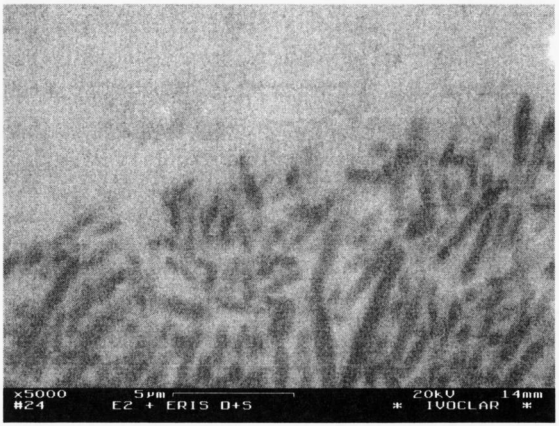

Fig 1. Two sintered glass-ceramics as a composite material for the fabrication of metal-free three-unit dental bridges. The framework material consists of lithium disilicate glass-ceramic and the veneer of apatite glass-ceramic. SEM

2.5 ZrO_2 glass-ceramics

The incorporation of ZrO_2 into glass-ceramics represents a particular challenge. ZrO_2 is known to be a particularly effective nucleating agent together with TiO_2 in glass-ceramics exhibiting minimal thermal expansion coefficients /2/. At the same time ZrO_2 sintered materials are known to demonstrate particularly high strengths.

In the composition range of 42 to 59 wt% SiO_2, 4-15 P_2O_5, 7-15 Li_2O, 15-28 ZrO_2 and additives /10/, the formation of a glass-ceramic with a main crystal phase of $Li_2ZrSi_6O_{15}$ was achieved. This crystal phase reinforces the glass-ceramic so that strengths up to 160 MPa can be achieved while the material remains translucent. Therefore, with a glass-ceramic from the SiO_2-P_2O_5-Li_2O-ZrO_2 system, composite materials consisting of a high-strength ZrO_2 and a sintered glass-ceramics can be achieved. In dentistry, these materials are used to fabricate core build-ups around ZrO_2-dental posts.

3. Conclusion

Sintered glass-ceramics are important components of many biomaterials systems. By carefully selecting the chemical composition and taking advantage of the different nucleation and crystallization mechanisms, tailor-made materials can be produced, which can be further developed to fabricate composite materials.

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