

THERMAL AND CHEMICAL PROPERTIES OF A GLASS IN THE SiO₂–CaO–F SYSTEM FOR DENTAL APPLICATIONS

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Abstract

The crystallization behaviour of a glass in the SiO₂–CaO–F system was analyzed using differential scanning calorimetry (DSC), X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). Three crystalline phases were detected according to ICDD patterns. The first phase formed at 583°C was identified as CaF₂. The morphology was spherulitic with a diameter of approximately 100 nm. The second phase was formed at 664°C. It was identified as calcium fluoride silicate 'Ca₂SiO₂F₂' (ICDD 35-0002). SEM investigation showed that the crystals were spherulitic with a diameter smaller than 100 nm. The crystals were precipitated in the volume of the glass and homogeneously distributed. As a third phase, cristobalite crystallized at 895°C.

The simultaneous release of calcium and fluorine ions from the vitreous glass in lactate buffer solution at pH 4.0, simulating an acidic oral environment, was investigated using X-ray photoelectron spectroscopy (XPS). The release of calcium and fluorine ions is of special interest for dental applications. The atomic ratios of the components Si, Ca and F at the glass surface after different leaching periods were determined. In order to investigate the leaching process, concentration profiles were measured using ion beam sputtering with Ar⁺-ions. The dependence of the atomic ratios of Si, Ca and F on the sputter time was determined in order to measure the depth of the leaching layers. Most probably, the release of calcium and fluoride was controlled by a surface layer rich in calcium and fluorine ions which dissolved with increasing leaching time. After 2 min leaching, a fluoride-rich surface layer measuring approximately 10 nm was detected. The atomic ratios of Si, Ca and F were different from the bulk composition ratios in a surface reaction layer of 800 nm thickness. After 30 min leaching time, a calcium- and fluoride-rich surface layer approximately 50 nm thick was formed. The bulk composition was reached at a depth of approximately 500 nm. The main component in the surface layer, after 12 days leaching in acidic environment, was silicon.

Keywords: calcium fluoride silicate, calcium release, crystallization, dental application

Introduction

Inorganic-organic composite materials used in dentistry for tooth restoration have a polyphase microstructure. The composite structure is formed by a polymer matrix in

which glass, glass-ceramic or ceramic fillers and other inorganic substances are embedded. The inorganic fillers mainly influence the mechanical properties of the composite, such as strength, modulus of elasticity, hardness and wear behaviour. In order to get highly aesthetic restorations, the inorganic components have to be transparent or translucent and their refractive index has to be adapted to the polymer matrix to avoid light scattering. In addition to the function of strengthening and the aesthetic demands, glass fillers can also fulfill further functions. An important chemical function of the inorganic filling components can be the release of specific ions like fluoride F⁻ and calcium Ca²⁺ ions. Fluoride and calcium hamper demineralization of tooth structure and also promote the remineralization of leached tooth structure [1]. Fluoride plays a key role in caries prevention [2–5]. The natural tooth structure, in the form of hydroxyapatite (HAP), becomes more durable against acid attack through the incorporation of the released fluoride. The tooth structure is then transformed into the fluorapatite structure. Fluoride also inhibits bacterial growth and has therefore a cariostatic effect [6]. Fluoride can be released from a fluoride containing salt embedded in the polymer matrix or directly from a glass filler containing fluoride. Most modern dental composites release fluoride. The release of calcium in acidic environment leads to an alkaline reaction near the glass surface, besides the effect of remineralization of the tooth structure. The buffer effect hampers secondary caries in the interface of restoration and tooth.

The aim of this work was the investigation of the thermal and chemical properties of a glass in the SiO₂-CaO-F system. The crystallization process was investigated using differential scanning calorimetry (DSC) and X-ray powder diffraction (XRD). The microstructure of the resulting glass-ceramic was investigated using scanning electron microscopy (SEM). The chemical composition at the glass surface after leaching was analyzed using X-ray photoelectron spectroscopy (XPS) [7–10]. The simultaneous release of calcium and fluoride from the glass surface was investigated on single-phase glass samples without polymer components. Concentration profiles for Si, Ca and F of leached glass surfaces were obtained by ion beam sputtering the samples with Ar⁺-ions.

Materials and method

Sample preparation

The glass was homogeneously melted using raw materials SiO₂, CaCO₃, M₂CO₃ and CaF₂. The melting temperature was 1250°C. The atomic ratios of Si, Ca and F in the bulk composition were 38.5 Si, 36 Ca, 25.5% F. The alkaline content was between 1 and 8%. The glass was produced as a frit. Bulk glass samples were heat treated at 550°C for 2 h and then slowly cooled in a furnace to room temperature.

The bulk samples were broken in small pieces for the DSC measurements. XRD room temperature measurements were conducted on powdered samples. Therefore, three bulk glass samples were heat treated at temperatures according to the exotherms of the DSC measurements. The heating rate was 1 K min⁻¹. The first sample was heat

treated at 595°C for 1 h. The second sample was heat treated at 675°C for 5 h. The third sample was heat treated at 910°C for 5 h. After the heat treatment, the glass-ceramic was ground to a fine powder for XRD-measurements. SEM investigations were conducted on etched fracture surfaces of the heat treated glass samples. For XPS measurements, bulk glass samples were fractured to get fresh surfaces measuring approximately 25 mm². The XPS samples were not polished in order to avoid surface contamination with the polish suspension.

Thermal analysis

The DSC measurements on bulk samples were conducted using a Netzsch DSC404 with platinum containers and nitrogen as atmosphere. The heating rate was 1 K min⁻¹ from room temperature to 1000°C.

The crystalline phases were analyzed using a Bruker D5005 (AXS). Room temperature measurements were conducted with heat treated and powdered samples. SEM investigations were done using a DSM962 (LEO GmbH).

XPS-analysis of the atomic ratios of Si, Ca and F

The fractured surfaces were leached in a lactate buffer solution with pH 4.0 at room temperature for different periods. The leached glass surfaces were analyzed after a leaching time of 2 min (sample B), 30 min (sample C) and 12 days (sample D). The atomic ratios of Si, Ca and F in the bulk composition as a reference sample was measured on a freshly fractured glass surface without leaching. In order to get information on the concentration profile of Si, Ca and F after leaching, the surface was sputtered with Ar⁺-ions of 1.5 keV kinetic energy. The estimated sputtering rate for this glass was approximately 2.5 nm min⁻¹. The maximum sputter time was 400 min. XPS was performed on an OMICRON Full Lab system. The analysis were carried out with non-monochromatized MgK_α radiation (h_v=1253.6 eV). The X-ray source was operated at 200 W (10 kV, 20mA). Element concentrations were evaluated from peak areas after Shirley background subtraction using theoretical cross sections [11].

Results

Differential scanning calorimetry

The heating curve to an end temperature of 1000°C for a bulk sample showed three exotherms and one endotherm. The exothermic peaks were located at 583°C (-29.5 J g⁻¹), 664°C (-103.4 J g⁻¹) and 895°C (-14.7 J g⁻¹). An endothermic peak occurred at 994°C (Fig. 1).

The crystalline phases appearing at 583°C, 664°C and 895°C were analyzed using XRD on heat treated and powdered samples. The main crystalline phase formed at 583°C was identified as CaF₂ (ICDD: 35-0816). The second phase formed at 664°C was identified as calcium fluoride silicate 'Ca₂SiO₂F₂' (ICDD: 35-0002). The

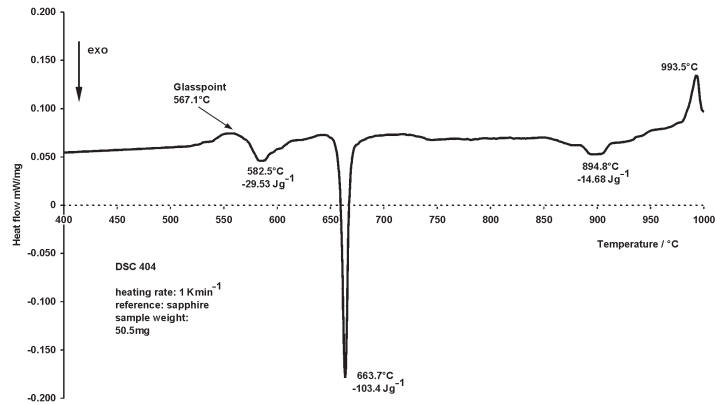


Fig. 1 DSC curve of a bulk glass sample from room temperature to 1000°C (heating rate 1 K min⁻¹)

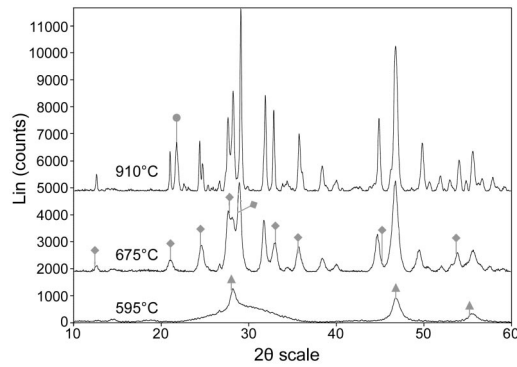


Fig. 2 XRD patterns of heat treated and powdered samples; ▲ – CaF₂ (ICDD 35-0816),
◆ – Ca₂SiO₂F₂ (ICDD 35-0002), ● – Cristobalite SiO₂ (ICDD 39-1425)

pattern of cristobalite (ICDD: 39-1425) matched to the XRD-peaks of the third phase crystallized at 895°C (Fig. 2).

The morphologies of the main crystalline phases developed at 583°C and 664°C are shown in the following SEM figures (Fig. 3).

XPS-analysis of the glass

Atomic ratios of Si, Ca and F in the bulk composition

The alkaline component and oxygen were not considered in the following XPS results. The composition of the glasses given in % are referred to as 'atomic ratios'. The %-values of the components Si, Ca and F are therefore not equivalent to their absolute content.

The atomic ratios of Si, Ca and F of the bulk composition were determined on different samples using XPS with different ion-beam sputtering rates (Table 1).

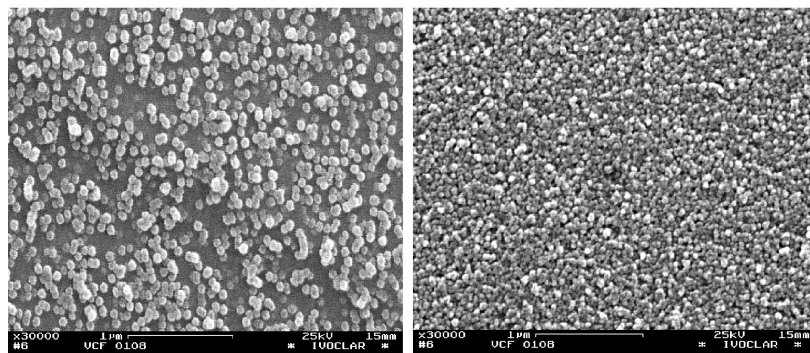


Fig. 3 Spherulitic morphology of crystals after heat treatment at 595°C for 1 h (left) and 675°C for 5 h (right) (fracture surface, etched with 3% HF solution for 10 s)

Table 1 Comparison between different XPS analysis of the atomic ratios of Si, Ca and F for bulk samples sputtered for different times

	Si/%	Ca/%	F/%
Sample A (not leached) Ar ⁺ sputtered for 10 min	33	39	28
Sample B (2 min leached) Ar ⁺ sputtered for 360 min	39	41	20
Sample C (30 min leached) Ar ⁺ sputtered for 270 min	37	42.5	20.5

The theoretical atomic ratios of the bulk composition were 38.5% Si, 36% Ca and 25.5% F. The XPS values were very close to the calculated concentration.

Atomic ratios of Si, Ca and F of glass surfaces leached in a lactate buffer at pH 4.0

The atomic ratios of Si, Ca and F were analyzed on the surface after different leaching periods (Fig. 4).

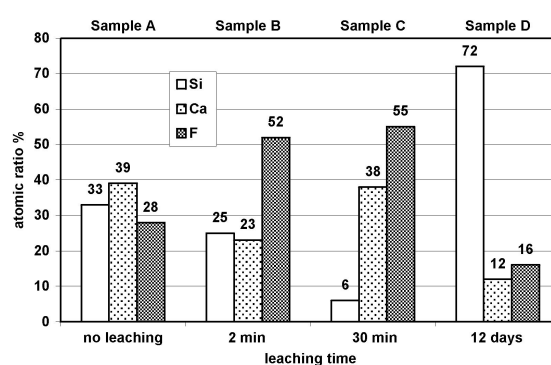


Fig. 4 The atomic ratios of Si, Ca and F determined by XPS of glass surfaces leached in a lactate buffer (pH 4) for different periods

The relative fluoride content at the glass surface increased remarkably after 2 min leaching (sample B) from 28 to 52% (+86%) in comparison to the content in the bulk composition (sample A). After 30 min leaching (sample C), the fluoride content was still on a high level of 55% (+96%). After 12 days leaching (sample D), there was still fluoride detectable. The content decreased to 16% (-43%). The relative calcium content at the glass surface decreased after 2 min leaching from 39 to 23% (-41%). After 30 min leaching, the concentration was comparable to the value of 39% before leaching. A remarkable decrease was detected after 12 days leaching. The concentration was 12% (-69%). The silicon content decreased after 2 min leaching from 33 to 25% (-24%). After 30 min leaching, the Si-content decreased to 6% (-82%). After 12 days leaching the glass surface was rich in Si because of the dissolution of Ca and F. The Si content measured 72%. This was an increase in comparison to the starting concentration of 118%.

XPS-sputter profiles of glass samples leached in a lactate buffer at pH 4

Sputter profiles of leached glass surfaces were taken in order to investigate the leaching process of calcium and fluoride (Figs 5–8).

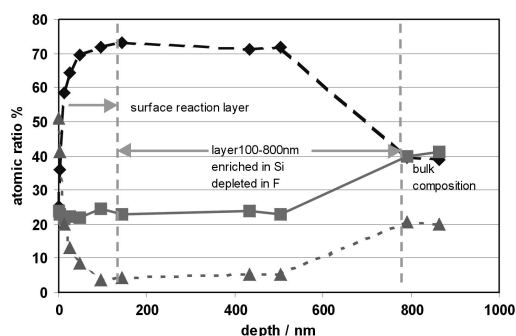


Fig. 5 Sputter profile of Si, Ca and F from sample B leached for 2 min in a lactate buffer at pH 4.0 (ion beam sputtering with Ar⁺, estimated sputter rate of 2.5 nm s⁻¹); ♦ – Si, ■ – Ca, ▲ – F

The surface reaction layer was approximately 100 nm in thickness. In this layer there was a change in the relative concentration of fluoride from 51 to 5%. The calcium content in this surface layer remained relatively constant at 25%. The silicon content in the surface reaction layer changed from 20 (surface) to 72% at a depth of 100 nm. The bulk atomic ratios of Si, Ca and F (Si: 39, Ca 41, F: 20%) were reached at a depth of approximately 800 nm. This depth was reached after 360 min of ion-beam sputtering with Ar⁺-ions with a sputtering rate of approximately 2.5 nm min⁻¹. The concentration of calcium was nearly constant at 22–24% from the surface to a depth of 500 nm. Then the concentration increased to the bulk composition value of 41%. The concentration profile of fluoride showed a characteristic course. The surface layer had a high content of fluoride (51%). The concentration decreased rapidly to a value of 5% at a depth of 100 nm. It was then constant to a depth of a 500 nm. Then, the fluoride concentration increased con-

stantly towards the bulk composition of 20% at a depth of 800 nm. The concentration profile of Si started at a low value of 25% at the surface. Then the concentration increased remarkably to 73% at a depth of 100 nm. This value was constant to a depth of 500 nm and then decreased steadily to the bulk composition value of 39%.

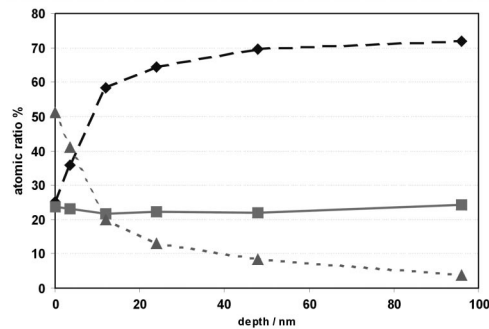


Fig. 6 Detail of the sputter profile of Si, Ca and F from sample B leached for 2 min in a lactate buffer at pH 4.0; \blacklozenge – Si, \blacksquare – Ca, \blacktriangle – F

The detailed concentration profile in the surface layer shows that the outermost 10 nm thick layer was enriched with fluoride and showed a remarkably low content of Si. In deeper layers, the Si content increased steadily while the fluoride content decreased to 5% at a depth of 100 nm. The concentration profile of calcium was constant at 20–25% to a depth of 100 nm.

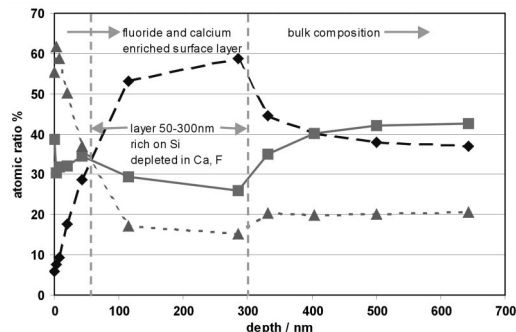


Fig. 7 Sputter profile of the atomic ratios of Si, Ca and F of the sample C leached for 30 min in a lactate buffer at pH 4.0; \blacklozenge – Si, \blacksquare – Ca, \blacktriangle – F

After 30 min leaching, the surface was enriched with fluoride and calcium, while the relative Si-concentration was remarkably decreased. The atomic ratios in the surface layer were 6% Si, 39% Ca and 55% F. The reaction layer rich in calcium and fluoride, but depleted in Si, was approximately 50 nm in thickness. At a depth of 50 to 300 nm, there was a region depleted in calcium and fluoride, and rich in silicon. The concentration profile of Ca decreased from 39 at the surface to 26% at depth of 300 nm. The concentration profile of fluoride decreased from 55–60% at the surface

to a constant value of 15% at depth of 300 nm. The concentration of Si increased in this region from 9 to 59%. At a depth of 300–650 nm the atomic ratios of Si, Ca and F reached the bulk composition ratio.

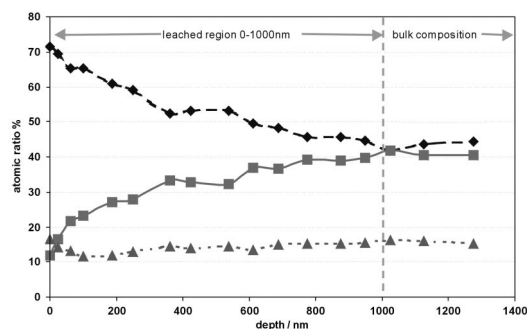


Fig. 8 Sputter profile of the atomic ratios of Si, Ca and F of the sample D leached for 12 days in a lactate buffer at pH 4.0; \diamond – Si, \blacksquare – Ca, \blacktriangle – F

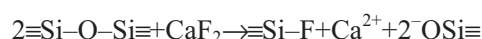
The atomic ratios of Si, Ca and F in the outermost surface layer after 12 days leaching were 80% Si, 10% Ca and 9% F. The surface was depleted in calcium and fluoride, but rich in silicon in comparison to the bulk composition. The Ca-content increased continuously with increasing sputter time. At a depth of 800 nm, the value of the bulk concentration of Ca was reached. The Si-content however continuously decreased from the surface into the bulk of the sample. At a depth of approximately 1 m the bulk concentration of 42% was reached. The fluoride content was quite constant over the whole sputter profile. The concentration ratio was in the range of 11 to 16%, which is below the bulk concentration of 20–28%.

Discussion

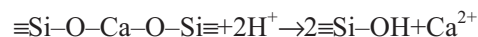
The crystallization behaviour of the first formed phase CaF₂ (ICDD 35-0816) was mainly influenced by the mobility of fluoride ions in the low temperature region. The crystallization of CaF₂ began approximately 17°C after passing the glass transition point at 567°C. The morphology of the crystals was spherical with a diameter of approximately 100 nm. The precipitated crystals were homogeneously distributed in the volume of the glass. The heat treated samples were transparent and opalescent. The second crystalline phase precipitated at 664°C was identified as calcium fluoride silicate 'Ca₂SiO₂F₂' (ICDD 35-0002). The morphology of this phase was also spherical with diameters smaller than 100 nm. CaF₂ was still detected at this temperature. The sample was transparent and opalescent despite the high content of crystalline phases. According to the DSC heating curve, a third phase was formed at 895°C. This phase was identified as cristobalite SiO₂ (ICDD: 39-1425). Cristobalite was not detectable in the SEM investigation of the sample heat treated at 910°C. The sample was white and showed some translucency.

The leaching process was investigated in advance of the XPS measurements by analyzing the leaching solution after different leaching periods. It was found that the leaching of fluorine ions reached maximum rate within 30 min of leaching. Therefore the XPS measurements were conducted on samples leached for 2 and 30 min. In comparison, a sample leached for a longer time (12 days) was also analyzed.

The surface analysis and the sputter depth profiles showed that the release of calcium and fluorine ions was most probably controlled by the formation of a surface layer enriched with these ions. After 2 min leaching at pH 4.0 an approximately 20–30 nm thick layer was formed with a high content of fluoride (sample B). The concentration profile of fluoride decreased rapidly to 10% at a depth of 100 nm. At a depth of approximately 500 nm, the fluoride concentration began to increase again and at a depth of 800 nm, it was similar to the bulk concentration. After 30 min leaching (sample C), an approximately 50 nm thick surface layer, enriched with Ca- and F-ions, was formed. The atomic ratios of fluoride was 50–60 and of Ca 30–40%. In this surface layer the concentration of Si was low (6–20%) in comparison to the bulk concentration (sample A). The detection of the calcium- and fluoride-enriched surface layer in samples B and C leads to the assumption that the release of Ca- and F-ions was controlled by the formation of a Ca and F enriched surface layer which started to grow immediately after immersing the glass surface into the leaching solution. This surface layer was dissolved with further leaching time. After 12 days leaching (sample D), Si was the dominant element in the surface layer. Calcium and fluoride were leached to a depth of approximately 1 μm. The calcium content was below the bulk concentration to a depth of 1 μm. The fluoride content in this 1 μm layer was also below the value of the bulk concentration. The lack of calcium and fluoride was a result of the leaching process. The release of fluoride was also investigated by the analysis of the fluoride content in the leaching solution of glass powder immersed in a lactate buffer at pH 4.0. There was strong agreement with the XPS elemental analysis that the main portion of fluoride was released within the first 30 min. After 30 min, the release rate remained constant. The glass-structure could have an important influence on the reaction mechanism for the simultaneous release of calcium and fluoride. The glass structure of the CaF₂ modified network could be described as [7]:



In this modification, Ca²⁺ could be easily removed by ion exchange with 2H⁺ existing in aqueous solution as H₃O⁺. Another possible reaction mechanism for the Ca²⁺ release in a silica network could be described by the ion exchange process [12]:



The removal of the comparatively large modifier ions leaves space for the further diffusion of H⁺ and H₂O.

The release of fluoride could be explained through another model. The glass structure described by the molecular dynamic simulation of microsegregation in alkaline earth fluoride silicate glasses [7] suggests that calcium and fluoride ions incorporated in an oxide glass can exist as clusters: CaF₂ → Ca²⁺+2F⁻ (clusters). The alkaline

earth ions form channel-like clusters. The existence of such clusters without strong chemical bonding to the network could explain the excellent leaching properties of this glass for calcium and fluorine ions. The glass-structure and the chemical bonding of the elements in the leached layer and in the bulk of the glass will be objectives for further investigations in order to describe the reaction mechanism of the leaching process. The XPS elemental analysis showed that the investigated glass composition had the potential to release calcium and fluorine ions in a lactate buffer at pH 4.0 simulating acidic environment in a clinical sense. A new effect of the glass investigated in this work, in comparison to conventional dental glass fillers, was the simultaneous release of calcium and fluoride when immersed in acidic environment.

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