Microstructure of Mica Glass-Ceramics and Interface Reactions between Mica Glass-Ceramics and Bone

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INTRODUCTION

The first machinable glass-ceramic, which contains mica as main crystal phase is MACOR® which was developed by Beall et al. (1971). The composition of the base glass is 47.2 SiO₂, 8.5 B₂O₃, 16.7 Al₂O₃, 14.5 MgO, 9.5 K₂O and 6.3 F.

A special method of controlled nucleation via phase separation and crystallization of silicate glasses has been used by Beall et al. (1971) to precipitate fluorophlogopite, namely KMg₃(AlSi₃O₁₀)F₂ as main crystal phase. The result was a glass ceramic which could be machined with standard metal working tools. Because of the combination of favorable properties, such as machinability and electrical isolation, very interesting technological applications can be considered. In order to ensure good machinability the precipitated mica crystals in the glass matrix need an optimal size and contact with each other. The material is machinable because of the preferred cleavage of the micas. Beall (1979) called the microstructure of the glass ceramic a "house of cards structure", which describes the orientation of the micas in the glassy phase.

Based on this development of Beall et al. (1971) further mica glass-ceramics (e.g., Beall, 1991) have been developed also for medical applications. The authors of the present paper review these developments (see chapters "glass-ceramic of DICOR®-type", "precipitation of micas rich in Ca²⁺-ions").

Further mica type glass-ceramics for technical purposes have been developed by Vogel et al. (1973) in the magnesium-aluminosilicate base glass system. Based on these investigations, the authors of this paper developed a phlogopite-type glass ceramic for medical application. This glass ceramic is biocompatible but not bioactive (see chapter "glass-ceramic of BIOVERIT® II-type").

The development of bioactive biomaterials has strongly been influenced by Hench et al. (1972) who developed the biomaterial BIOGLASS® from the SiO₂-Na₂O-CaO-P₂O₅-F system. The new biomaterials show bioactive properties and the materials are bonded to living bone. BIOGLASS® forms apatite on the surface.
in contact and reaction with the body fluid and the living bone. On the basis of the knowledge of this apatite formation in BIOGLASS®, further bioactive glass-ceramics, containing apatite crystals, have been developed (Blencke et al., 1977; Strunz et al., 1978).

Kokubo et al. (1982) showed a preferred bonding of bone and apatite-wollastonite glass ceramic, and an additional apatite formation in reaction with simulated body fluid could be shown on the surface of the biomaterial (Kokubo et al., 1990).

The authors of this present paper developed a machinable bioactive glass-ceramic consisting of two crystal phases, namely mica and apatite, and a glassy phase. The microstructure and the properties, especially the interphase reactions between mica and bone are presented (see chapter "BIOVERIT® I-type glass-ceramics"). Other glass-ceramics containing micas and phosphates are reviewed (see "glass-ceramics containing micas and CaO-, P2O5-additives").

**Glass-Ceramic of DICOR®-Type**

(Mica Glass-Ceramic)

Grossman (1972, 1983) crystallized glasses consisting essentially of 45-70 % SiO2, 8-20 % MgO, 8-15 % MgF2, 5-35 % R2O and RO; where R2O consists of K2O, Rb2O and Cs2O and RO consists of SrO or BaO and other alkaline earth oxides. Additions, such as ZrO2, Al2O3 and colourants were used. These investigations have been the basis for the development of a glass of the composition (in weight percent): 60.9 SiO2, 0.6 Al2O3, 17.1 MgO, 13.8 K2O, 4.9 F, 4.7 ZrO2, 0.05 CeO2 (Adair, 1984). CeO2 can give the glass-ceramic fluorescence. This glass was heat treated and the microstructure was investigated by scanning electron microscopy (SEM) (Grossman, 1989; Adair, 1984).

Grossman (1989) showed that the base glass is phase separated and mica crystals of KMg2.5Si4O10F2− type grow during heat treating the glass from 625 to 1075 °C. A typical microstructure is shown in Figure 1 (the preparation technique is indicated in the caption of the Figure). The glass ceramic shows excellent properties, such as machinability, translucency and good bending strength. Hence, the material is used in dental medicine as crowns.

**Glass-Ceramics of BIOVERIT® II-Type**

(Mica Glass-Ceramic)

The crystallization behavior of magnesium-alumino-silicate base glasses was investigated by Vogel et al. (1973). Na2O, K2O and F were added to SiO2-Al2O3-MgO-glasses and the mica precipitation has been studied. Based on these results, Höland et al. (1981) analyzed the phase formation processes in glasses of the composition: 43-50 SiO2, 26-30 Al2O3, 11-15 MgO, 7-10 R2O, 3.3-4.8 F, 0.01-0.6 Cl, 0.1-3 CaO, 0.1-5 P2O5, wherein R2O is the sum of 3-5.5 wt. % Na2O and 4-6 wt. % K2O. A new type of phlogopit in a curved shape was precipitated in a glass ceramic. The formation of this new phlogopite was investigated in a glass with the chemical composition (wt. %): 44.5 SiO2, 29.9 Al2O3, 11.8 MgO, 4.2 F, 4.4 Na2, 4.9 K2O, 0.1 CaO, 0.1 P2O5, 0.1 Cl by TEM and SEM (Höland et al., 1991a). The chemical composition of this new curved mica, (Na0.18K0.82)(Mg2.24Al0.61)(Si2.78Al1.22)O10.10F1.90 could be analyzed by energy dispersive spectroscopy (EDS) (Höland et al., 1991a).

In comparison to glasses which form flat mica crystals, the control of the reduced phase separation process allowed the formation of the new curved mica crystals (Höland et al., 1981). Because of a low concentration of nucleating centers, curved micas and cordierite crystals (as secondary crystal phase) grow in the range 700-1050 °C. The phase formation and the structure of curved mica crystals, that are typical for glass-ceramics of BIOVERIT® II-type, have been studied in comparison to flat crystals (Vogel and Höland, 1982; Höland et al., 1983b; Elsen et al. 1989). Crystal structure investigation by X-ray diffractometry of phlogopite micas showed that the curved mica has a still higher content of aluminum ions in the octahedral coordination.

Small glassy phase separated droplets are the nucleating centers of the curved phlogopite. Curved phlogopites grow as isolated ball shaped aggregates (Figure 2). The crystallization up to 980 °C can be controlled so that the curved crystals come into contact with each
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The experiences of the surgeon (Beleites et al., 1988) showed that middle ear implants have to have a very good machinability, that means a high content of curved micas (Beleites et al., 1988) and dental products should show a special translucency.

Precipitation of Micas Rich in Ca²⁺-Ions

Silicate glasses rich in CaO were developed by Ehrt and Heidenreich (1978), and Kasuga and Kasuga (1991). A characteristic composition which has been investigated by Ehrt and Heidenreich was 50 % SiO₂, 18 % Al₂O₃, 7 % MgO, 10 % CaO, 3.5 % Na₂O, 4.5 K₂O, 7 Ma. % F. Kasuga and Kasuga (1991) could get glass-ceramics of the composition 43.5 SiO₂, 12.7 Al₂O₃, 25.5 MgO, 6.5 CaO, 1.7 K₂O and 10.1 F. The main crystal phase is a mica rich in Ca²⁺-ions and secondary phases, such as diopside, anorthite, richterite and others were precipitated in the glass-ceramic (Kasuga and Kasuga, 1991).

Developments of Ehrt and Heidenreich (1978) and Kasuga and Kasuga (1991) to increase the CaO-content in mica type glass-ceramics had given the possibility to develop machinable glass ceramics with high mechanical strength (bending strength 210-300 MPa). The microstructure of the glass ceramic formed by Kasuga and Kasuga contains mica and diopside crystals and a glass matrix phase. An application for dental crowns was proposed by Kasuga and Kasuga (1991).

BIOVERIT® I-Type Glass-Ceramics
(Mica-Apatite Glass-Ceramics)

A combination of different properties within a glass ceramic material, especially the combination of machinability and bioactivity was possible in multi-component glasses of the SiO₂-(Al₂O₃)-MgO-Na₂O-K₂O-P₂O₅-CaO system. Typical compositions are 35.9 SiO₂, 18.1 Al₂O₃, 6.5 MgO, 5.1 Na₂O, 4.0 K₂O, 16.7 CaO, 11.2 P₂O₅ and 2.5 wt. % F, or 38.7 SiO₂, 1.4 Al₂O₃, 27.7 MgO, 6.8 K₂O, 10.4 CaO, 8.2 P₂O₅ and 1.9 wt. % TiO₂ (Höland et al., 1983a, Höland et al., 1991a).

Mica-apatite glass-ceramics show a characteristic microstructure and phase formation reactions (Vogel and Höland, 1987). The base glass shows three glassy phases, a SiO₂-rich glass matrix, a CaO-P₂O₅-F-rich big droplet phase, and a Na₂O-K₂O-Al₂O₃-MgO-F-rich big droplet phase (Figure 6). Heat treating the glass at temperatures between 610 and 1050 °C allowed a double controlled in situ crystallization of mica and apatite. Apatite grows inside the CaO-P₂O₅-F-rich big droplet phase (Figure 7) and phlogopite formation is a result of a solid state reaction of the glass matrix phase and the small droplet phase (Figure 8). The apatite crystals of
Ca₅(PO₄)₂(OH,F)-type could be determined by X-ray diffraction measurements and the flat phlogopite crystals, (Na₀.2₁K₀.₈₁)(Mg₀.₅₂Al₀.₄₄)(Si₂.₈₀Al₁.₂₀)O₁₀.₁₈F₁.₈₂ could be analyzed by EDS (Höland et al., 1983 a, 1985).

The authors of the present paper assume that similar reactions take place in glasses containing low concentrations of Al₂O₃ (or Al₂O₃-free glasses). The difference between the phase formation in glasses shown in Figures 6-8 is that the phases formed are very small and the mica consists of KMg₂.₅(Si₄O₁₀)F₂-type.

Electron microprobe investigations carried out by Höland et al. (1991b) show a very good contact of mica-apatite glass-ceramic and bone. One year after operation, the reaction interface between bone (tibia of guinea pig) and mica-apatite glass-ceramic is less than 15 µm (Figures 9 and 10). Apatite is present within the biomaterial but an additional small calcium phosphate layer will be formed on the surface of the glass-ceramic. Secondary ion mass spectroscopy (SIMS) investigations show the tendency that phosphate groups become enriched at the surface of BIOVERIT® I glass-ceramics under simulated conditions (Höland et al., 1991b). Figure 11 shows that the peak positions 31, 47 and 63 are responsible for the enrichment of phosphate groups. Additionally an NaCl-rich layer from the simulated body fluid seems to be deposited onto the sample (position 35, 37).

The process of bioactivity seems to be of a complex nature. It includes solid state reactions (apatite-apatite reaction), ion diffusion processes (e.g. Na⁺-, Ca²⁺-diffusion), Ca-phosphate formation and a possible positive influence of silicates (Hench, 1991) on the bone regeneration reaction. This corresponds with results of bioactive behavior of glasses and glass-ceramics reported by Hench (1991), Kokubo et al. (1990), and Wilson (1991).

Glass-Ceramics Containing Micas and CaO, P₂O₅-Additives

Shibuya et al. (1990) also formed glasses by adding CaO and P₂O₅ to SiO₂-(Al₂O₃)-MgO-K₂O-F⁻ glasses, e.g.: 57.1 SiO₂, 11.7 MgO, 13 K₂O, 5.9 F, 4.8 ZrO₂, 3.1 CaO, 2.6 P₂O₅ and 1.84 CeO₂. The formation of different crystal phases was investigated by X-ray diffraction measurements (Shibuya et al., 1990).

Shibuya et al. (1990) developed a KMg₂.₅(Si₄O₁₀)F₂-mica glass-ceramic containing also calcium phosphate groups. Apatite crystals have been analyzed by X-ray diffraction measurement after heat treating the glass up to 1050-1075 °C. Shibuya et al. (1990) reported also, that they have carried out scanning electron microscopic measurements which show that the crystals are in close contact with each other, they are cross-linked.

Conclusions

The results of the authors of papers cited in the bibliography and the authors of this paper showed that mica glass-ceramics are biocompatible materials which can be used for bone substitution in medicine.

BIOVERIT®-type glass ceramic is used for dental restoration. Mica glass-ceramics of BIOVERIT® II-type and mica-apatite glass ceramics of BIOVERIT® I-type have been successfully applied in head and neck surgery and orthopaedic surgery in more than 600 patients (Schubert et al., 1988; Höland et al., 1990).

References


Mica glass-ceramics, structure and reactions


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**Figure 11 (above).** Negative secondary ion mass spectra (SIMS) of BIOVERIT® I glass-ceramic before (A) and after soaking (B) in simulated body fluid (SBF) at 95 °C for 64 hours.

**Figure 10 (at left).** Electron microprobe investigation of the interface between mica-apatite glass ceramic and bone (16 weeks after implantation).

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Discussion with Reviewers

Reviewer III: The paper reviews some material aspects of glass-ceramics that are considered by the inventors to be biocompatible. The biological behavior of this type of material is neither investigated, nor documented, nor published carefully enough!

Authors: The biomaterials which have been developed at Otto-Schott-Institute of Jena University are glass-ceramic of BIOVERIT® type. The biocompatibility of BIOVERIT® I-type has been investigated by J. Gummel, T. Schubert, K.J. Schulze and W. Purath and are documented in qualification thesis of orthopaedic clinic, Dresden, Germany and partly in the text reference Schubert et al., 1988. The biocompatibility of BIOVERIT® II-type is shown by E. Beleites, University Jena, clinic for otorhinolaryngology and the results are documented in his qualification theses and partly in text reference Beleites et al. (1988), and in Vogel and Höland (1987).

The well established cell culture test method was utilized for the determination of toxicity for both ceramic types. Neither the "bioactive" ceramics nor the "bioinert" reference materials demonstrated a significant influence on the cellular activity (proliferation).

Additional testing protocols are documented in the references listed previously. We have also performed further biocompatibility studies with laboratory animals: Sixteen weeks after subcutaneous implantation of Bioverit I, with its higher solubility, a stabilization of the cellular reaction was observed. The investigators concluded that this result can be interpreted as a sign of controlled surface solubility factors and excellent biocompatibility.