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Future perspectives of biomaterials for dental restoration

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Abstract

The development of biomaterials that can be used to substitute metals in dental restorations represents the main challenge of future research activities until the year 2020. Therefore, the authors will focus on the presentation of two types of biomaterials for dental restoration: glass-ceramics and sintered ceramics. Dental biomaterials must have a highly aesthetic appearance that is comparable to that of natural teeth. Furthermore, they must be more durable than natural teeth and show good mechanical properties at ambient temperatures.

Based on the state of the art and the latest research activities, the presentation is focused on glass-ceramics with high toughness, glass-ceramics with optical properties comparable to those of natural teeth and glass-ceramics that are processed with preferred techniques, for example, those which are moulded on different types of high-strength substrate materials. In addition, high-strength and high-toughness materials such as lithium disilicate glass-ceramics can be processed either by moulding or by a new method, that is, machining. Possible directions will be presented for moulding different types of glass-ceramics such as fluoroapatite containing glass-ceramics on high-toughness substrates made of glass-ceramics or very tough sintered ceramics.

The focal point of this presentation is the demonstration of the high-strength and high-toughness sintered ceramics of the ZrO_2 type. The preferred processing method of this type of biomaterials for dental restoration is machining using CAD/CAM technologies. Future activities will be focused on improving the quality of the ZrO_2-type biomaterial. At present ZrO_2 ceramics are white opaque. One of the main aims is to achieve optical properties comparable to those of natural teeth in ZrO_2 ceramic. Therefore, the material has to be developed in special dental colours with the same mechanical properties and good durability as that of the white ZrO_2. The authors will show future directions for developing coloured ZrO_2 sintered ceramics.

Future research activities will be focused on gaining a better understanding of the phenomena and mechanisms of toughening glass-ceramics and ceramics. With the acquired knowledge on the toughening mechanisms, new directions for developing ceramics until the year 2020 will be explored. The technology to achieve this goal will be applied nanotechnology.

Keywords: Glass ceramics; Ceramics; High toughness; Dental materials; Dental restoration; Esthetics; Colour

1. Introduction

Patients throughout the world are showing a growing interest in restorative dental materials, which enable natural teeth to be faithfully recreated with regard to their function and aesthetic appearance. In today's fast-paced, work-intensive and challenging world, many people are changing to a more healthy lifestyle and they want a good-looking smile to match it. Nevertheless, in some situations, the destruction of tooth structure is inevitable and teeth have to be restored or replaced. There are many different causes (apart from avoidable hygiene problems) for the loss of tooth substance, which range from disease to trauma. As a result, dental restorations are still in demand, even today. The spectrum of dental restorations ranges from small restorations such as inlays and veneers to large restorations such as dental crowns and bridges. The latter are preferably secured on natural teeth. Furthermore, a trend has emerged towards implant-supported restorations, particularly in the replacement of single teeth. Ceramic materials are in demand for this entire range of dental restorations. At this point, it has to be emphasized that the success of biomaterials in human medicine is determined by the clinical long-term clinical success. Important aspects of clinical success are the properties of biomaterials (especially strength, toughness, abrasion behaviour comparable to natural

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teeth, translucency, colour, durability) and the processing technologies (moulding, machining, sintering).

Based on the successful long-term use of glass-ceramics and sintered ceramics, these materials show the most promise for the development of new materials up to the year 2020. Consequently, this presentation will primarily deal with these two groups of materials.

The developments up to 2020 will have to take certain important factors into account. In restorative dentistry, PFM restorations are still widely used. With the growing trend towards metal-free dental restorations, however, the situation will change. This represents a considerable challenge for any future developments.

2. Glass-ceramics are time-tested materials

Special attention in the development and application of glass-ceramics for dental restorations was given to the combination of properties which are typical for both ceramics and glasses. On the other side, the moulding technology used in glass processing with nearly no shrinkage preferred this application of glass-ceramics. With the development of mica glass-ceramics by Malament and Grossmann[1] and Adair and Grossman[2] glass-ceramics entered the field of restorative dentistry. These materials gained acceptance in this field because of their exceptional translucency and appropriate strength and above all their favourable processing properties. For example, advantage was taken of the viscous flow phenomenon, which is typical for glasses as well as glass-ceramics, to achieve certain shapes by centrifugal casting. At this early stage of development, a second preferred processing method was identified for these materials: The precipitation of mica crystals allowed the glass-ceramics to be machined.

After the centrifugal casting process had been successfully tested, glass-ceramics were developed, which could be used to mould dental restorations by employing the lost wax technique. This technique also took advantage of the viscous flow of glass-ceramics. This technology was presented for leucite-based glass-ceramics by Wohlwend and Schärer[3] and Rheinberger[4] at the end of the 1980s/beginning of the 1990s. This type of glass-ceramics is produced according to a special reaction mechanism involving controlled surface nucleation and crystallization (Höland et al.[5]). The leucite crystals ($KAlSi_2O_6$) grow in the base glasses of the SiO_2–Al_2O_3–K_2O–Na_2O materials system. The crystals are for the most part precipitated in the glass matrix in isolated form, with the exception of some twinning as shown in Fig. 1. This materials system is characterized by particularly favourable chemical durability. In addition, the glass-ceramics exhibit a long viscosity curve which allows the moulding process to be conducted over a relatively wide temperature range. This moulding technique enables the dental technician to achieve outstanding fit of the dental restorations. The exceptional properties of leucite glass-ceramics were first presented in IPS Empress®. These properties included lifelike translucency, high strength of 150–180 MPa, fracture toughness as the K_{IC} value of 1.3 MPa m$^{0.5}$ and good wear resistance (Dong et al.,[6] Heinzmann et al.,[7] Apel et al.[8]). Because of these favourable properties and the dedicated moulding technique, IPS Empress® glass-ceramics were used as 32 million units over in the fabrication of inlays and onlays (particularly for restorations in the anterior region) between 1991 and 2007 (Höland et al.[9]). Clinically controlled studies by Edelhoff et al.,[10] Brodbeck[11] and Fradeani and Redemagni[12] in particular have shown a success rate of more than 95% for these indications in clinical applications of up to 11 years.

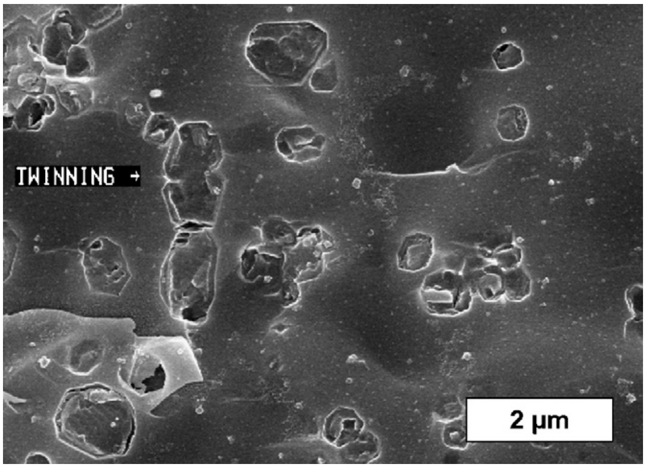

Fig. 1. Precipitation of leucite, $KAlSi_2O_6$, in a glass matrix. The crystals are isolated from each other, some twinning is visible. SEM, etched sample. Reproduced with permission from Höland, Beall, Glass-ceramic technology, The American Ceramic Society, all rights reserved, 2002.

On the basis of the successful results achieved with leucite glass-ceramics of the Empress type, it is anticipated that these materials will continue to be used for the fabrication of dental inlays, veneers and single dental crowns in the long term. Consequently, it is expected that commercially available biomaterials which have been studied over a period of more than 10 years and have benefited patients a million times over will continue to be successfully used for the next 12 years, that is, until 2020.

In addition to the moulding technique, machining using CAD/CAM technology has emerged as another popular processing technique for glass-ceramics of the IPS Empress type. As mentioned earlier, mica glass-ceramics were the first glass-ceramics in dentistry that could be mechanically processed. In the meantime, intensive research, has shown that leucite glass-ceramics can also be machined. The glass-ceramic IPS Empress® CAD is a case in point. This material allowed metal-free restorations to be fabricated for a patient chairside in one short appointment. The main indications included inlays and dental crowns. As this technology together with the favourable properties of leucite glass-ceramics offers many advantages, above all time savings for the dentist and patient, it is to be expected that these applications will grow in popularity until 2020.

In order to enable glass-ceramics to be used in the fabrication of dental bridges (preferably three-unit bridges) and for single crowns in the molar region, the strength and toughness of these materials had to be increased. As a significant increase in these parameters could not be achieved in leucite-based glass-ceramics, a new materials system had to be developed.

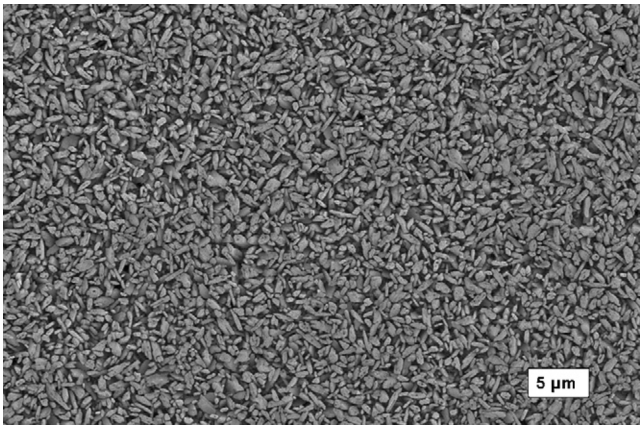

Fig. 2. Interlocking microstructure of lithium disilicate glass-ceramics. The crystals are in close contact to each other. SEM, etched sample.

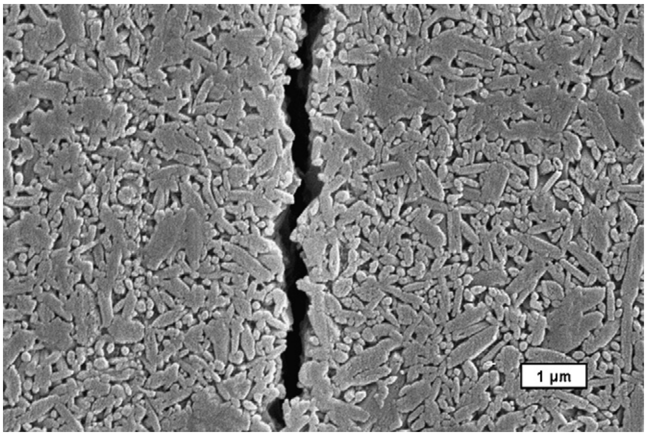

Fig. 3. Crack propagation in lithium disilicate glass-ceramics. The fracture occurs in the glass matrix and propagates around the crystals. SEM, etched sample.

Glass-ceramics of the lithium disilicate system showed a great deal of promise in this respect. Lithium disilicate glass-ceramics were developed by Stookey,[13] Beall,[14] Freiman and Hench[15] in multicomponent glass systems. Initially, the materials system SiO_2–Li_2O–P_2O_5–La_2O_3–ZnO–Al_2O_3–K_2O was developed for the product called IPS Empress® 2 (Höland et al.[16]). Subsequently, the materials systems SiO_2–Li_2O–P_2O_5–ZnO–Al_2O_3–K_2O (Bürke[17]) and SiO_2–Li_2O–P_2O_5–ZrO_2–Al_2O_3–K_2O (Apel et al.,[18] Höland et al.[19]) were developed for the IPS e.max® products. High flexural strengths of more than 500 MPa as well as high fracture toughness with K_{IC} values of 2.3 to approx. 3 MPa $m^{0.5}$ can be achieved with the last-mentioned glass-ceramic systems. The ZnO-free system containing ZrO_2 allows the optical properties to be selectively controlled (translucency without additional opalescence). As a result, the material is suitable for use in restorative dental applications. In contrast, the other systems frequently produce uncontrolled opalescent effects during the crystallization process.

A study on the fracture behaviour of glass-ceramics conducted by Apel et al.[8] and Höland et al.[20] clearly showed that the heightened strength and toughness compared with other glass-ceramics, for example, leucite glass-ceramics, is produced by the special microstructure of the interlocking crystals (Fig. 2). This microstructure causes an induced fracture to absorb more energy by forcing cracks to propagate around each individual lithium disilicate crystal in the glass matrix. This phenomenon increases the fracture toughness. Apart from its high-strength and toughness, the material demonstrates excellent translucency, despite the high crystal content and the interlocking of the crystals (Fig. 3).

These lithium disilicate glass-ceramics can be used for both the moulding and the machining technique involving CAD/CAM methods. However, neither the base glass nor the lithium disilicate end product is suitable for machining in commercial dental CAD/CAM equipment. The base glass is too brittle and the crystal content of more than 60 vol.% of the end product is too high for this processing method. Therefore, an intermediate product, a lithium metasilicate glass-ceramic, was developed for this purpose. This glass-ceramic contains dendritic crystals, which allow the material to be machined quickly and easily. Because of its particular composition and microstructure, lithium metasilicate glass-ceramic is blue in colour. Tooth-coloured dental restorations are fabricated by machining the blue intermediate product and subsequently heat treating the restoration at 850 °C. Despite the fact that the lithium metasilicate phase disintegrates and the new lithium disilicate phase crystallizes during the heat treatment process, the dental restoration does not undergo any perceptible change in volume. Hence, the fit of the product is not affected. Glass-ceramics of the IPS e.max® type are additionally veneered with a fluoroapatite glass-ceramic (Schweiger[21]) to imitate the optical properties of natural teeth as closely as possible. These glass-ceramics contain needle-like fluoroapatite crystals that grow along the *c*-axis in the glass matrix. A secondary phase at the interface of the crystal and the glass matrix has not been observed (Höland et al.[22]).

Initial clinical studies of up to 5 years on the glass-ceramics of the IPS e.max® System show a very low failure rate of up to 3.3% for the application of dental crowns and small dental bridges (Edelhoff,[23] Anusavice[24]). As a result of this success rate as well as the favourable combination and the use of two fundamentally different processing methods and the wider indication range compared with leucite glass-ceramics, the forecast until 2020 for this group of materials involving lithium disilicate glass-ceramics that are veneered with other types of glass-ceramics, e.g. fluoropapatite glass-ceramics, is very good. This is based on the assumption that mechanical processing with CAD/CAM methods will continue to grow in popularity. At the same time, it must be emphasized that lab-side processing techniques, which involve different coating methods to achieve highly aesthetic results, offer very attractive development potential.

3. Sintered ceramics of the highest toughness

Although glass-ceramics allowed to combine a variety of properties of glass and ceramic materials, it was not possible to achieve the highest toughness and strength parameters of ceramics. Therefore, high-strength materials came into play for dental restoratives. As early as in the 1990s, high-strength type $3Y_2O_3–ZrO_2$ sintered ceramics were used as restorative materials in dentistry because of their high toughness of approx. 4–5 MPa $m^{0.5}$. They were used to fabricate dental posts in particular. In order to secure the post in the root canal, a glass-ceramic of the $Li_2ZrSi_6O_{15}$ type was pressed on the ZrO_2 post in a process that corresponds to the mentioned moulding technology. This structure on the ZrO_2 post served as the abutment. Subsequently, a metal-free restoration, for example, made of glass-ceramic, was placed on the abutment (Schweiger et al.,[25] Höland and Beall[26]).

With the further development and improvement of CAD/CAM technology, ZrO_2 sintered ceramics were developed for long-span dental bridges in particular (Studart et al.[27]). Rothbrust[28] showed that a selectively produced openpred ZrO_2 ceramic can be successfully machined, for example, with the CEREC® equipment from Sirona. In the subsequent thermal treatment, the dental restoration is densely sintered at 1450 °C. Shrinkage is controlled in the process, which ensures the precision fit of the finished product. The ZrO_2 framework of the restoration is veneered with a fluoroapatite glass-ceramic (Schweiger[21]). Even though the ZrO_2 sintered ceramic demonstrates a lower translucency than glass-ceramics, a highly aesthetic appearance similar to that of natural teeth is achieved with the veneer. For this purpose, the white opaque sintered ceramic is coated with a coloured liner before the veneering ceramic is applied.

These tough sintered ZrO_2 ceramics could be further developed and improved by imparting them with tooth colours. Should it become possible to fabricate tooth-coloured restorations with these ceramics, the application of a liner would become superfluous. At the same time, the optical properties and aesthetics of dental restorations would be further enhanced. Until now, it has not been possible to colour these dental ceramics, as the addition of pigments causes uncontrolled crystal growth, which adversely affects the fundamental properties of the materials. However, the application of fluidized bed technology has

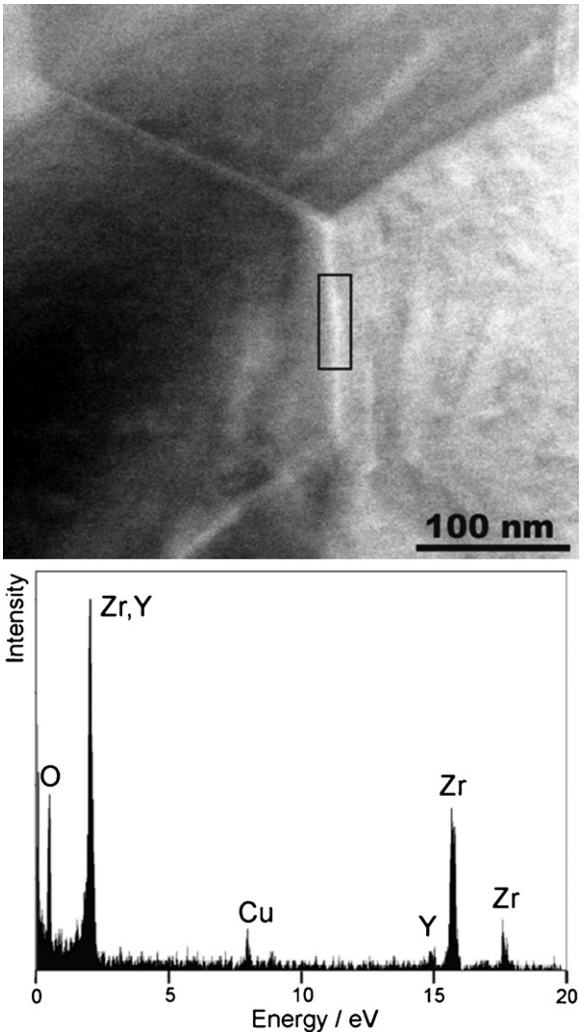

Fig. 5. High-angle annular dark field (HAADF) STEM image of the $Y_2O_3–ZrO_2$ ceramic containing 1 Mass% Pr_2O_3. The EDX spectrum of the outlined area shows the presence of yttrium and zirconium oxide. The signal of Cu is due to stray radiation from the holder.

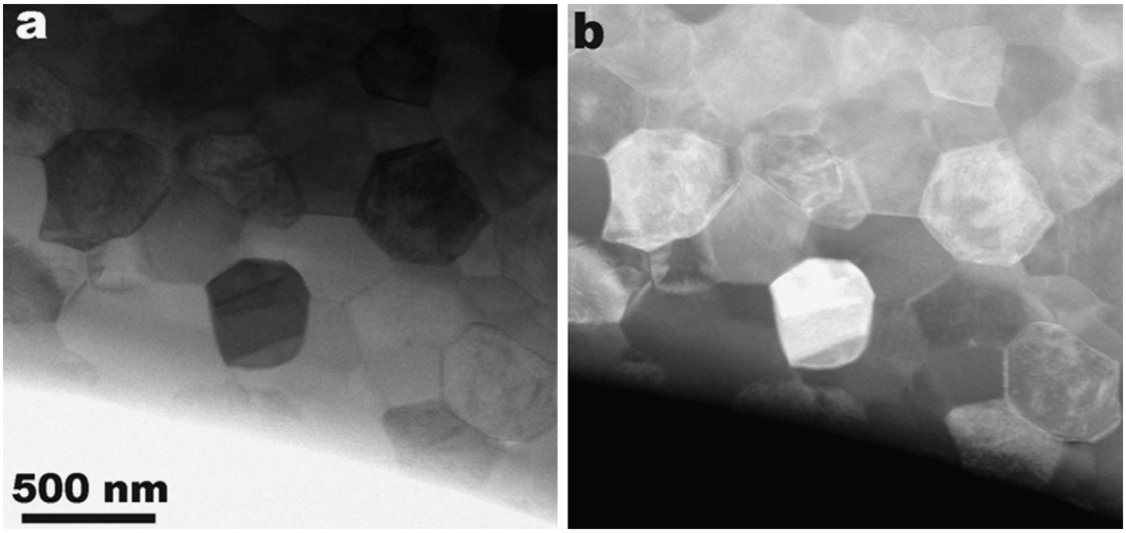

Fig. 4. (a) Bright field (BF) and (b) annular dark field (ADF) STEM images of a $Y_2O_3–ZrO_2$ ceramic containing 1 Mass% Pr_2O_3. Microcrystals with a diameter between ca. 100 and 500 nm are recognizable.

enabled the ions of the d- and f-elements to be incorporated to produce homogenous colouring of ZrO_2 in suitable dental shades.

The incorporation of Pr^{3+} in an undisturbed ZrO_2 crystal lattice, that is, without the addition of Y_2O_3, is described by Bondioli et al.[29]. They demonstrated that even with a content of 10 mol.% Pr_2O_3, ZrO_2 is incorporated into the lattice and the tetragonal modification is maintained.

The authors of this paper have undertaken initial studies to analyze the effect of the ions of the f-elements in type $3Y_2O_3–ZrO_2$ dental ceramics. In order to achieve the desired dental shades, contents of this f element of oxide in the ppm region up to a few tenths of wt% are preferably used. However, in order to clearly recognize a possible effect of the added oxides, a significantly excessive Pr_2O_3 concentration of 1.0 wt% was incorporated. It should be noted here that as a matter of convention the content of the additional ions is expressed in terms of oxides.

The following experimental procedure was used to analyze the 1.0 wt% Pr_2O_3 containing $3Y_2O_3–ZrO_2$ sample: Scanning transmission electron microscopy (STEM) was performed on a Tecnai F30 microscope (FEI; field emission cathode, operated at 300 kV) equipped with an energy dispersive X-ray spectroscopy (EDXS) detector (EDAX). Qualitative analysis was done by selecting small areas in the STEM image and recording an EDX spectrum there.

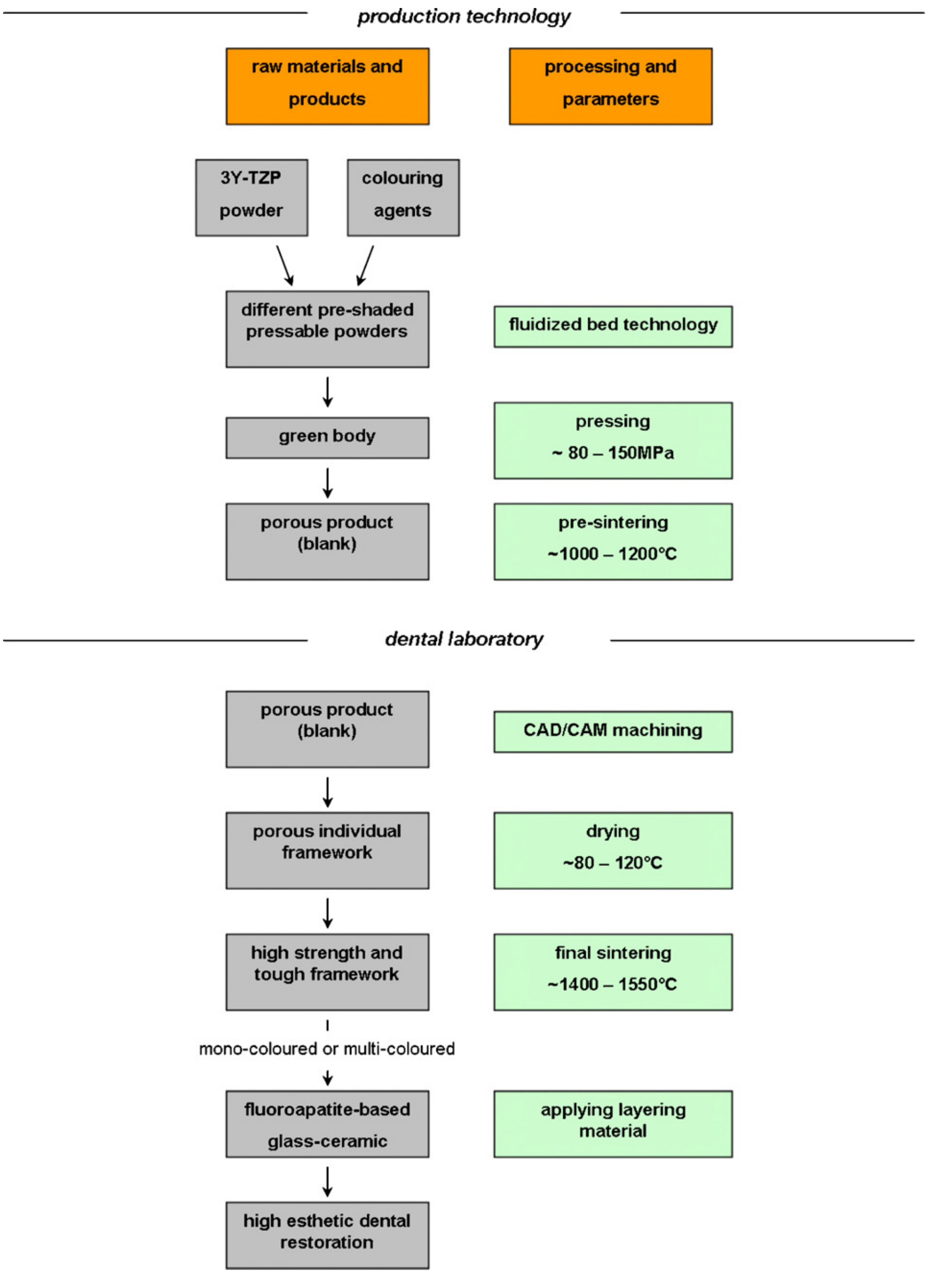

Fig. 6. Possible scheme of processing coloured ZrO_2 ceramics.

The specimen preparation started with cutting rectangular a piece (approximately 1.5 mm × 1.5 mm × 15 mm) from the ceramic. After embedding it in a Cu pipe (diameter ∼ 3 mm), ∼300 μm thick discs were cut. These disks were ground and polished on both sides to a thickness of 100–150 μm, and subsequently a dimple was ground on one or both sides to reach a thickness in the center of 20–30 μm. In the final step, milling with argon ions (PIPS, Gatan) was performed until a hole in the center of the samples was formed.

The main results of the TEM study were focused on determining the microstructure formation and ion distribution in the sample. The microstructure of the Y_2O_3–ZrO_2 ceramic was characterized by STEM investigations (Fig. 4). The crystallites are clearly recognizable in both BF and ADF-STEM images. Their size varies in the range of 100–500 nm with an average of ca. 400 nm. The interface region between the crystallites appears with bright contrast in the HAADF-STEM image shown in Fig. 5. An EDXS analysis of this region shows the presence of Zr and Y oxide. No praseodymium could be detected; neither there nor in the EDX spectra recorded from other crystal regions (not shown here). This observation indicates that Pr might be distributed homogeneously in the sample so that the Pr content is everywhere below the detection limit of the EDXS method. Moreover, irregular crystal growth does not occur. Therefore, a homogenous microstructure is produced. As a result, the toughness of the coloured end product is not adversely affected compared with the white ZrO_2.

In summary, no accumulation of this type of ion could be observed either at the interface or in the crystals. Furthermore, secondary phase formation was not established either in the STEM or the XRD investigation. The EDX-TEM analysis of the interface between two crystals did not reveal any accumulation of Pr^{3+} ions.

These initial colouring results achieved in Y_2O_3–ZrO_2 dental ceramics show that colouring is possible in principle. However, it is clear that additional fundamental research is necessary to establish the solid state reactions that are necessary for colouring the materials. A possible processing is shown in the scheme of Fig. 6. The ceramics developed in this way will be used as biomaterials in the near future and will be of significance up to the year 2020. One special example of a multicoloured framework of a dental bridge is shown in Fig. 7.

Fig. 7. Framework of a multi-coloured three-unit dental bridge of ZrO_2.

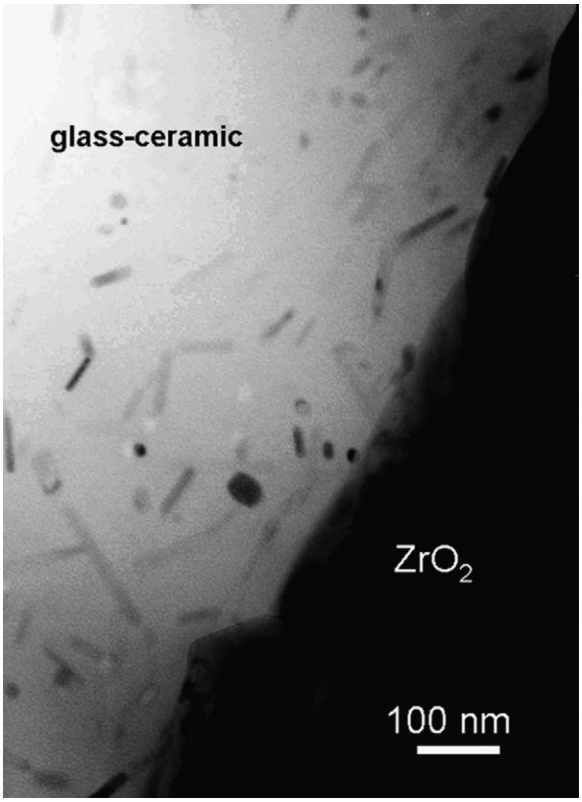

Fig. 8. Bond between a fluorapatite glass-ceramic and a very tough ZrO_2 ceramic. TEM.

4. Fundamental phenomena of toughening and joining ceramics

Future directions will be focused on developing high-strength and high-toughness ceramics and glass-ceramics with improved optical properties (translucency and colour). In addition, the fusion of both types of materials will become a special focus. This requires fundamental research on glass-ceramics and ceramics on investigating the mechanisms involved in strengthening and in increasing the toughness of these materials. The basis of the studies on sintered ceramics were conducted by Rühle and Evens[30] and Deville et al.[31] on the martensitic transformation in ZrO_2 ceramics. The new findings will enable important conclusions to be drawn on the development of new ceramics up to 2020. The entire spectrum of potential ceramics showing high-strength and high toughness has been shown by Kelly and Denry[32]. In this context, the extent to which the principles of nanotechnology can be used must be addressed.

Apart from the fundamental principles of materials development, the issue of joining different materials plays an important part in ensuring the successful use of biomaterials in restorative dental applications. The problem of joining and connecting different glass-ceramics has been resolved for the most part. However, there is still room for improvement. Sintered ceramics and glass-ceramics can also be successfully joined. Fig. 8 shows an example of how a ZrO_2 sintered ceramic and an apatite glass-ceramic have been joined. Nevertheless, the technical processes need to be optimized, particularly the thermal processes in the fabrication of stress-reduced veneering materials with controlled internal stresses.[33]

Finally, another topic in the research field of joining needs to be addressed, that is, the cementation of dental restorations on natural teeth or implants. This part of the restorative procedure is vital to the successful application of biomaterials in dentistry. The development of improved adhesive systems or the utilization of biological mechanisms will represent a considerable challenge until the year 2020. Furthermore, suitable materials must be developed for fabricating abutments similar to those used in conventional metal systems.

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