Zirconium oxide is used in several industries, e.g. in the nuclear industry, for the manufacture of grinding beads, hydrogen sensors, knife blades, optical fibre links or for hearing aids, finger and hip prostheses\(^1\). It has been used in the field of medicine since as early as 1969, initially in the field of orthopedics. It was first used in dentistry in the early 80s. Its establishment in the field of dentistry was hampered for many years by the fact that it was not possible to shape zirconium oxide using the classic manufacturing methods in dentistry. Today, there are very many dental indications for zirconium oxide, extending far beyond prosthetic restorations. It is used for example for abutments, implants and orthodontic brackets\(^2\). This article is based on an interesting study which sought to coordinate using the veneering ceramic ceraMotion® Zr (Dentaurum Ceramics) with the framework material zirconium oxide Nacera® (Doceram Medical).

**Modern zirconium oxide in dental technology**

There are many reasons for the high level of acceptance of zirconium oxide. Some of the main points are the increased demand for all-ceramic restorations and the advantages these bring, e.g. they are aesthetic, biocompatible and free of metal. The mechanical characteristics of zirconium oxide make it possible to manufacture complex restorations and long-span bridges. In comparison to systems using a combination of metals and ceramics, zirconium oxide offers good aesthetic characteristics. In addition, the supragingival margin line can prevent damage to the soft tissue. Within a short period of time, zirconium oxide has changed thanks to the advantages it brings from being an alternative to metal to being ideally suited as a material for monolithic restorations. The possibilities for coloring zirconium oxide have also been developed further - from using the dipping technique or coloring using powders to techniques which make use of a brush to give the frameworks a very precise, individual coloring (aquarelle method) (Fig. 1a to c).

**The manufacturing process of zirconium oxide**

The raw material for zirconium oxide is zircon (ZrSiO\(_4\)). The mineral is extracted using a chemical procedure and converted with the help of diverse additives into zirconium oxide. Zirconium oxide (zirconium dioxide) is a pure polycrystalline ceramic of high density and is characterized by a lack of the glass phase change. Different mineral ingredients and organic binding agents are added when shaping the powder form into granulates. It is the binding agents that allow the so-called atomization: the conversion of a liquid solution (zirconium oxide powder and binding agent) into a powder with globular-shaped agglomerates (Fig. 2).
The veneering ceramic material must be compatible with zirconium oxide as a framework material, as is the case for example with the ceramic material ceraMotion® Zr (Dentaurum, Ispringen, Germany). This synthetic ceramic belongs to the new generation. Its manufacture begins with the melting of highly pure ingredients at 1500 °C. The base glass is then rapidly cooled (water-cooling) to prevent crystallization and to harden the liquid into a solid glass material. At this stage, it is a non-crystalline solid material (glass). Its opacity can be regulated by adding a material such as Zr02 or Ti02. The manufacturer colors the material at various stages throughout manufacture by means of a thermal procedure (heat treatment for several hours at approx. 1000 °C/1832 °F). This helps stabilize the physical-chemical characteristics. The color shade and the expansion coefficient of the ceramic materials remain stable even in the case of many firings during manufacture.

**Note:** Since the initial composition of ceraMotion® Zr contains no feldspar, problems known to arise from different compositions can be avoided. The dental technician benefits from a level of quality that remains constant throughout each individual batch.

**The transparency of modern zirconium oxide restorations**

There is a wide range of zirconium oxide materials. Their opacity varies according to their chemical composition and the mechanical characteristics have changed with values ranging from sometimes more than 1400 MPa (classic zirconium oxide) to 600 MPa (transparent zirconium oxide).
Fig. 5 — Opacity of different groups of ceramic materials. The opacity varies slightly depending on the color.

Fig. 6 — Mechanical flexural strength of different materials for all-ceramic frameworks.

Zirconium oxide, in earlier days white and relatively opaque, is now available in many color shades and in different degrees of transparency. The transparency values are close to those for lithium disilicate.

**Note:** Light diffusion is a complex phenomenon based on the reflection and diffusion of light within the restoration. Good aesthetics are the result of an optimal adaption of transparency and shade between the framework and the veneering ceramic material. It is however extremely rare for a manufacturer of zirconium oxide to work closely together with a manufacturer of a veneering ceramic.

The high level of translucency is achieved by smaller-sized zirconium oxide grains and the integration of aluminum oxide. The aluminum oxide contained in the translucent zirconium oxide is distributed homogeneously in the shape of fine particles onto the zirconium oxide granules from the outside. Opaque zirconium oxide has aluminum oxide particles, which have been distributed inhomogeneously (Fig. 4).

**Influence of the changed level of translucency**

For a long time, the low level of translucency in zirconium oxide was seen as a deficit in the manufacture of aesthetic restorations. Some authors recommended experimenting with the firing cycles in order to increase the transparency. It is actually possible to witness the phenomenon of an increase in the grain size by increasing the firing temperature or the amount of time at a given temperature. Translucency increases as the amount of contact points between the grains decreases [3]. However, it is not advisable to alter the recommended firing temperatures as this can lead to a decrease in the mechanical strength and a marked decline in the hydrothermic aging resistance.
The new generation of zirconium oxide aims to deliver a translucency comparable to that of lithium disilicate without negatively affecting the mechanical characteristics of zirconium oxide. These materials can even be used for monolithic crowns in both the anterior and the posterior region (Fig. 10). Modern zirconium oxide has therefore become a serious competitor to lithium disilicate, more because it is easy to process and available at a competitive price (Fig. 5).

Note: Classic forms of zirconium oxide (flexural strength: 1000 to 1400 MPa) are deemed the only materials that may be used for restorations with four units in accordance with the international norm ISO 6872. Bear in mind: The good aesthetic characteristics of translucent zirconium oxide are due, amongst other reasons, to the increased proportion of the cubic phase. This results in a lower mechanical strength. It is therefore recommended to only use the modern, "cubic" zirconium oxides for bridges with a maximum of three units (Fig. 6).

Control of transparency

Since the translucency of monolithic restorations is not a result of the layering process, it must come from the material itself. Part of the light is reflected or absorbed in conventional veneering ceramics. These phenomena are diffuse and depend on the quality of the surfaces. It is therefore important to try to get the refraction index of the ceramics as close as possible to that of the natural tooth enamel. This is where ceraMotion® One Touch Concept comes in (Fig. 7).

CeraMotion® One Touch

The ceramic pastes for the manufacture of frames made of zirconium oxide are available from the ceraMotion® One Touch range as 2D and as 3D pastes. The 2D pastes are used to correct the shade and the color characteristics. The 3D pastes are used to replace conventional incisal pastes or to change the surface texture. The behavior of both masses during firing is remarkable. The tooth shape remains exactly the same (Fig. 8).

Both the composition of the pastes and the glass transition point of the low-fusing ceramic have been optimized. This prevents the well-known phenomenon of the material turning opaque during firing, thereby having no influence on the targeted transparency.

- Easy handling thanks to ready-mixed ceramic pastes.
- Set specially assorted for the finishing of aesthetic, fully anatomical restorations.
- Maximum aesthetics thanks to color-coordinated pastes with 3D effect.
- Small changes in shape and the adding of contact points are possible.

Significance of the coefficient of thermal expansion and the thermal conductivity

Coefficient of thermal expansion

The coefficient of thermal expansion for veneering ceramics and the zirconium oxide framework material must match to prevent fissures resulting from a thermal or mechanical shock. It is advisable to select a coefficient of thermal expansion for the veneering ceramics that is slightly under that of zirconium oxide (Fig. 9). This puts slight pressure on the veneering ceramics which has a positive effect on the durability of the restoration.

Thermal conductivity

The norm ISO 9693-2 was recently revised to include parameters showing resistance to thermal shocks. Behavior during a thermal shock is influenced by thermal conductivity. Thermal conductivity (λ) is by definition the property of a material to conduct thermal energy as heat by means of heat conduction. The higher the thermal conductivity, the better the material conducts the heat. The lower, the better the product can insulate. The thermal conductivity of zirconium oxide is extremely low in comparison to other materials (e.g. aluminum...
oxide, gold), thereby enabling, for example, the pulp complex to be isolated. This is an advantage in the case of fixed restorations on vital teeth. It is advisable to pay particular attention to the bond between the veneering ceramic and the framework in zirconium oxide. Frequently, the recommendation is made to increase the temperature for the firing of the first layering by 20 to 30 °C/ 68 - 86 °F. The aim of this is to ensure there is no sloughing in the area between the zirconium oxide and the veneering ceramic once the restoration has been put into the mouth.

**Note:** The quality of the bond between the veneering ceramic and the zirconium oxide depends on the chemical composition at the time of firing. The glass transition temperature (softening temperature) for ceraMotion® One Touch (485 °C/905 °F) supports bonding during firing at 730 °C/1346 °F.

**Fluorescent characteristics and coloring of the framework**

**Fluorescence**

Natural teeth are fluorescent in
black light \[7\]. In order to generate this light reaction, manufacturers add a mixture of fluorescent pigments based on rare earths to veneering ceramics. Zirconium oxide is not naturally fluorescent. Fluorescence describes the phenomenon of materials that can absorb and re-emit radiation energy from the spectral band of short wavelengths. The fluorescence of ceraMotion\textsuperscript{®} Zr is adjusted to perfectly imitate the fluorescent characteristics. This is true also for the materials used to treat the surfaces of monolithic zirconium oxide restorations. Pastes that are intensely fluorescent bring out the inherent fluorescence, in the knowledge that the spectrum of the fluorescence of tooth enamel changes as the patient grows older (Fig. 10 - 11).

**Coloring of pre-sintered zirconium oxide frameworks**

Zirconium oxide is colored using the aquarelle technique with color solutions, which contain metal ions such as iron, manganese, chromium, praseodymium etc. (Fig. 12). The coloring agents are a mixture of soluble substances whose molecule weight is high, such as for example polymers. The viscosity of the fluids is important for optimum penetration of the solution into the pores. The organic components in zirconium oxide are broken down during sintering. As temperatures subsequently increase, the reaction between the metal oxides and the zirconium oxide powder is supported. The composition of the metal ions and the viscosity of the solution influence the final color and its homogeneity. Each type of ion produces its preferred color (brown = iron, pale pink = neodymium, cream = cerium, orange = cerium, black = manganese, yellow = praseodymium). Coloring not only changes the shade, but also the opacity \[8\].
Note: There is a potential for the coloring liquids to react aggressively with the heating elements in the furnace. It is therefore advisable to dry the frameworks as much as possible before subjecting them to the final firing cycle. Iron chloride, contained in certain coloring liquids, could be the cause for the deterioration of the oven's durability due to the formation of hydrochloric acid (HCl).

Influence of zirconium oxide's inherent color

Various pre-shaded zirconium oxides have appeared on the market over the past few years. They clearly show deviations in color, even if the manufacturer claims they belong to the same color shade. Figure 13 shows color differences for the classic shade A3. One reason for this is that, to date, there has been little collaboration between manufacturers of zirconium oxide and manufacturers of the veneering ceramics. In this respect, the work done jointly by the research teams from Dentaurum Ceramics and Doceram Medical is remarkable since, by pooling their competence, they have optimized the aesthetics for zirconium oxide restorations. In order to bring spectrophotometrical readings together with visual observations, several color shades were mapped out which resulted in shades of zirconium oxide, which coordinate perfectly with the veneering ceramics (Fig. 13b and c).

Diverse indications: from frameworks for veneering to monolithic restorations

Bonding

When zirconium oxide was first available, the chipping of veneering ceramics was a matter of concern. There was a lot to learn about bonding veneering ceramics to frameworks. Tests carried out (ISO norm 9693-2) show considerable differences in the behavior of different materials (Fig. 14).

Nowadays, zirconium oxide can be used for many different indications, e.g. as a framework for restorations with a veneering, as a framework for minimal layer veneers or as a monolithic structure in need only of surface treatment with Stains or ceraMotion® One Touch 2D or 3D pastes (Fig. 15).

Hardness and surface abrasion

Zirconium oxide has a Vickers hardness value of 1250 (HV10) which is much harder than that of natural teeth. This led to many studies on the long-term risks of possible damage to opposing teeth. If the hardness is viewed as an element worthy of consideration, then abrasion would appear to be an equally important parameter. There are two differing opinions, one recommending the surface to be finely polished, whilst the other recommends using a veneering ceramic material (semi cutback or glaze). Glazing the surface (thin-layer veneer) involves completely covering the outer surface that greatly reduces aging and enables the natural tooth fluorescence to be copied.

Note: the veneering ceramic ceraMotion® One Touch (HV530) is much softer than zirconium oxide,
but abrasion in particular is lower in comparison to raw zirconium oxide.

The rougher the surface, the greater the wear on the opposing teeth. The following three images (Fig. 16a-c) compare the surface roughness of a veneering surface without treatment, a veneering surface that has been mechanically polished and a veneering surface with a fine glazing layer (ceraMotion® Zr). The application of a glazing layer clearly reduces the surface roughness and lends a degree of fluorescence as required.

Aging

The aging process of zirconium oxide has also been the subject of many scientific publications [9,10]. The diffusion of water into oxygen gaps leads to increased tensions which in turn lead to a transformation from the quadratic into the monoclinic phase. Crystallographic changes increase volume which leads to micro-crack formations and an increase in the roughness of the zirconium oxide surface (Fig. 17). This phenomenon is known as Low Temperature Degradation (LTD). If the zirconium oxide is covered with a layer of a veneering ceramic material, a physical barrier against potential damage is built. The veneer material must demonstrate a good resistance to chemical dissolution. Tests carried out on products with ceraMotion® One Touch showed values well below normal limits.

Patient cases from the Master Dental Technician Germano Rossi (Italy): The ceraMotion® One Touch Concept

In the following example, Germano Rossi milled the framework (anatomical tooth shape, slightly reduced in size) from shaded zirconium oxide (Nacera®) (Fig. 18). ceraMotion® One Touch 3D was used in the palatal region as a replacement for the classic incisal pastes. The classic stains and pastes from the ceraMotion® Zr series gave the restorations individual characteristics and the level of glaze required. In only a few steps, Rossi created the illusion of layering or one of a natural look (Fig. 19).

In the second example, Rossi used the zirconium oxide from Nacera® Pearl 3 and colored the framework after milling using the aquarelle technique. The fully anatomical tooth was slightly reduced in the buccal region (semi cutback) and given a veneering with the incisal and dentin pastes from the ceraMotion® Zr ceramic system. The dental technician completed the proximal areas and the palatal ridge with One Touch 2D and 3D pastes. The restoration then received a light coating of glaze (Fig. 20 - 21). The One Touch 3D pastes give the restoration a realistic 3D effect. This is thanks to the glass transition temperature (485 °C/905 °F) which is perfectly suited.

Note: The method shown could also be used for frameworks in lithium disilicate since the coefficients of expansion are similar.

Both the 2D and 3D pastes from the One Touch concept demonstrate a thixotropic behavior that enables them to bond well when applied despite the fact that the grain sizes of each paste differ. It is therefore easy to change the morphology of the restorations or to apply contact points. The transparency and the fluorescence of the pastes give an impression of vitality and depth.

Conclusions

Ceramic restorations are currently experiencing a paradigm shift. Two important parameters combined together are the cause for this shift:
1. There is a new generation of new ceramic materials, making us rethink conventional veneering techniques.

2. Digital techniques have found their way into the laboratories, unleashing a technological revolution.

As is always the case when far-reaching changes in work processes present themselves, those who benefit are the ones who are curious and interested in the developments and who adapt to the changes. The success of such a big change as the one currently happening in the field of all-ceramic restorations is based on a symbiosis of scientific competence in materials development, the application possibilities in practice and the resulting acceptance by dental technicians in the course of their daily work.

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