



High-tech Bioceramics – History and Present State

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In restorative dentistry, metal-ceramic has been a standard for fixed restorations since the 1960s. Since the mid-1990s the metal-to-ceramic alloys used for this type of restoration have increasingly been replaced by high-strength ceramics. Prominent among these is an yttrium-stabilised zirconia ceramic (zirconia Y-TZP [tetragonal zirconia polycrystals])^{1,2}. The starting material for this high-strength industrial ceramic is produced chemically from mineral raw materials (zirconium sand), partly stabilised with yttrium oxide and processed by the ceramic method into products and semi-finished parts. For dental applications, e.g. for dental laboratory products, blanks for crown and bridge frameworks are shaped with burs or diamond instruments³. Since the end of the 1990s the material also known as 'high-tech ceramic' has been increasingly used in dentistry instead of cast alloys. Oxide ceramics have been in clinical use in medicine, starting with aluminium oxide, since around 1970, and were initially used predominantly in orthopaedics as a component of replacement hip joints. Ceramic hip joints, also made from the newly developed high-performance material zirconia-TZP since the mid-1980s, are now widespread and safe to use because of their good biocompatibility, high fatigue strength and,

Summary

In restorative dentistry part of the crown and bridgework is produced from all-ceramic. The high-strength framework structures required are mainly made of oxide ceramics. Zirconia ceramic is currently gaining in popularity because of its good biocompatibility and fatigue strength. The first provider of such a zirconia was Metoxit. The company supplies either finished parts, such as posts, abutments and implants, or blanks which are further machined to produce posts, crown and bridge frameworks, for example by CAD/CAM technology. Looking at their past activities means also looking at the history of high-tech bioceramics in the various fields of medicine. The development and present application of this high-strength zirconia ceramic is outlined.

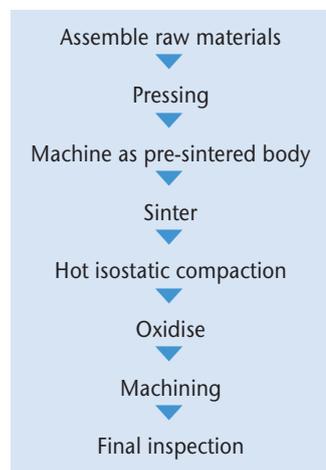
Key words

abutments; all-ceramic; alumina; implants; industrial ceramic; oxide ceramics; prosthodontics; zirconia

Introduction



Table 1 Manufacturing process of hot isostatic post-compaction ZrO₂-TZP²³



above all, outstanding wear properties. After appropriate testing and compliance with the prevailing standards, the 'bioceramic' materials alumina (aluminium oxide) and zirconia (zirconium oxide) are licensed for medical devices and are chosen depending on the indication range.

The Swiss company Metoxit AG was the first company that applied its knowledge of oxide ceramics to dentistry and is a trail-blazer and one of the market leaders in the manufacture and processing of these high-performance ceramics. Looking at their past activities means also looking at the history of high-tech bioceramics in the various fields of medicine. As a result of innovations in the processing technology applied to these ceramics, this company has succeeded in improving the quality and stability by using purer and purer raw materials, optimised manufacturing processes and the narrowest production tolerances in order to increase user safety and biological acceptance. Since 1986, applying the method known as 'hot isostatic post-compaction' (HIP) to bioceramics for medical use has made it possible to condense the ceramic material after the sintering process (Table 1). As a result, the strength and reliability of these materials is greatly increased⁴. This marks a milestone in the manufacture and development of oxide ceramics in medical technology.

Metoxit AG



Fig 1 Da Vinci chronograph from IWC Schaffhausen. A special series with casings made of zirconia ceramic was issued, then a world-first.

Metoxit AG is based in Thayngen, close to the German border in the Swiss canton of Schaffhausen. The company sees itself as a supplier of products made from specialist ceramics for various sectors of industry. Metoxit emerged in 1978 as a subsidiary of the company (then) Swiss Aluminium AG (Alusuisse) and the local ceramics firm Tonwerke Thayngen AG. The original tasks were the development and manufacture of materials for aluminium production. The name Metoxit was trademarked and registered in 1973, 5 years before the foundation of Metoxit AG. The AGZ group (AG Ziegelwerke Horw-Gettnau-Muri, Horw, Switzerland) took over Tonwerke Thayngen AG in 1985 and the Alusuisse shares in Metoxit AG in 1986. The Managing Director of Metoxit AG was Dr Wolfhart Rieger from the formation of the company until 2004, when he was succeeded by his long-standing colleague Dr Wolfram Weber.

As a manufacturer and supplier of oxide ceramics, Metoxit AG initially concentrated on alumina, followed by zirconia. By introducing and thoroughly testing high-tech ceramic materials and by using innovative production methods, the company has attained a unique position in the field of medical technology. Today, Metoxit AG sells more than half of its products in the orthopaedic and dental sectors. Together with its sister company Saphirwerk Industrieprodukte AG (SWIP) in Brugg, Switzerland, it supplies leading orthopaedic firms with ceramic hip joints and manufactures a wide range of superior wearing parts for industry, e.g. pistons and plungers for high-pressure pumps. As partners of the world-renowned Schaffhausen clock company IWC, Metoxit AG developed and produced the world's first watch cases in zirconia ceramic in 1986 (Fig 1). Nowadays Metoxit AG, together with SWIP, employs 150 people at two locations and is continuing to expand with new innovations (www.metoxit.com).

Oxide Ceramic in Orthopaedics

Since 1980, the use of oxide ceramics in orthopaedics has been pursued intensively by Metoxit AG. The possibility of their clinical application was tested by various companies from the 1960s onwards and advanced by fundamental research until about 1970. Further

development of alumina led to its clinical use in orthopaedics around 1970, as ball-heads and later inserts for acetabular cups for hip joints. Up to the end of the 1990s the oxide ceramics had been continually improved, especially in terms of mechanical properties, by the use of refined raw materials combined with innovative production methods. Another key step proved to be the introduction of the above-mentioned HIP process (1986) by Metoxit AG. As a result, the flexural strength and long-term life expectancy of alumina and, since 1986, zirconia were considerably improved.

Metoxit gained Food and Drug Administration (FDA, USA) approval with the Master File for alumina as early as 1989 and with the Master File for zirconia in 1991. In 1993 authorisation from the French and EU health authorities was obtained, both after extensive studies and animal experiments lasting two years. The Master Files were an international leap forward for Metoxit, especially with the material zirconia-TZP, and they are regarded as the standard by other manufacturers in this field⁵. At the same time, as materials were being developed, the machining methods and manufacturing precision were continuously being improved. For instance, the surface of alumina and zirconia, e.g. for orthopaedic ball-heads, can be polished to a roughness depth of $0.002\ \mu\text{m}$ (value Ra). To achieve this, the know-how of SWIP was essential. The accuracy of sphericity of ball-heads, which is obtained in the proprietary process of SWIP, is $0.1\ \mu\text{m}$. Finished parts for dental technology or prosthodontics/implantology can also be manufactured by Metoxit AG with extremely high accuracy (Fig 2)⁵. This information about the quality of specific products is presented in the context where individual clinical long-term problems are being discussed in the field of ball-heads of hip joints. Presently, the wear characteristics of zirconia (Y-TZP) articulating against itself are being investigated and discussed. The wear rate and clinical experience emphasises that medical-grade zirconia, in some products, has been critical to low-temperature degradation for the use in hip prostheses. A close look has to be given to the different products that are available. The quality can vary a significantly among products of different manufacturers⁶.



Fig 2 Ball-heads and acetabular cup inserts for artificial hip joints made of oxide ceramics.

Zirconia ceramic has been used for a few years in orthodontics⁷ for brackets and in prosthodontics for root posts⁸ and abutments⁹. Metoxit AG started to move into the field of dental materials with root posts made of zirconia, which were produced from 1991 onwards. The key to their success was the hardening and tempering of the material by the HIP process, so that Metoxit soon held something of a monopoly in the area of root posts. The advantage of the 'Metoxit process' is that root posts can be manufactured with very small diameters (as low as 1.4 mm), very narrow tolerances and high resistance to fracture. To date this quality has not been matched either by injection moulding methods or by extrusion (Figs 3 to 5).

Abutments made from zirconia, which can be precisely adapted to or fitted into implants, has emerged as another area of production. From 1995, abutments (Zirabut) made of zirconia were developed by the Liechtenstein dental technician, Arnold Wohlwend, and produced by Metoxit, initially for experimental work on titanium implants (Figs 6 to 10)⁹⁻¹¹. Later, abutments were manufactured which were mounted onto a tita-

Introduction of Zirconia into the Dental Sector



Fig 3 Example of a product: root post made of zirconia ceramic.

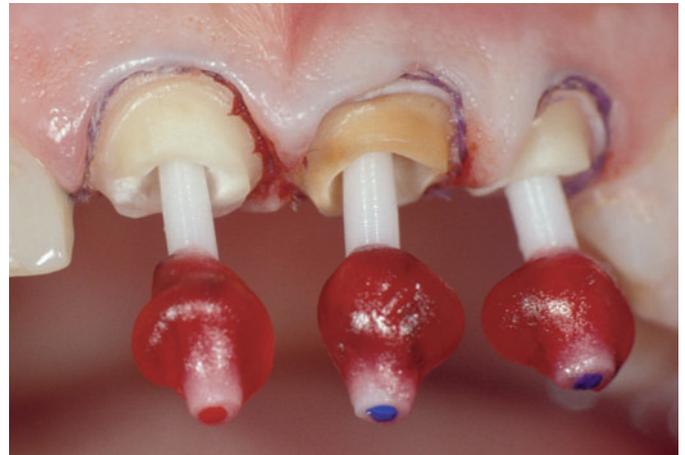


Fig 4 Root posts made of zirconia ceramic in the root canals for the build-ups. Clinic: Dr Guido Heydecke, Freiburg.

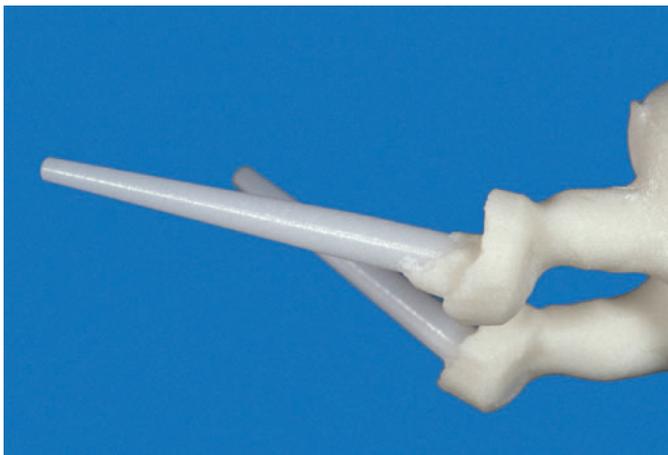


Fig 5 The root posts can be fitted with ceramic build-ups by using the press technique.



Fig 6 First prototypes of abutments made of zirconia ceramic created by Wohlwend in 1995.

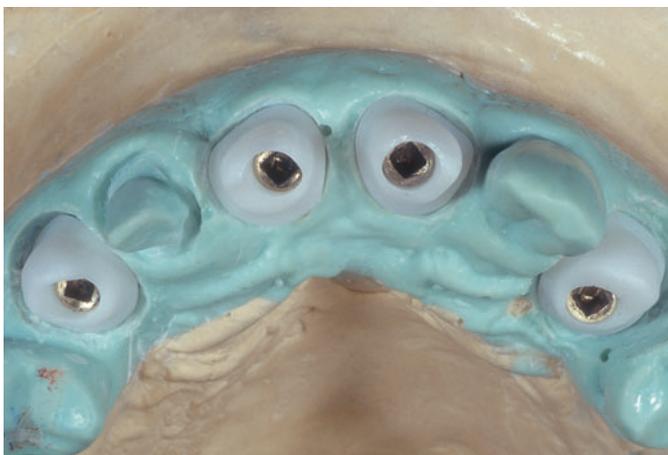


Fig 7 First case study involving the clinical use of abutments made of zirconia ceramic from 1995, by Wohlwend.



Fig 8 The zirconia abutments in the mouth fixed on the implants. Clinic: Dr Stefan Studer at the Dental Institute in Zürich.



Fig 9 The abutments and prepared teeth were fitted with all-ceramic crowns. Tooth 22 is a natural tooth.



Fig 10 Patient with occlusal view.

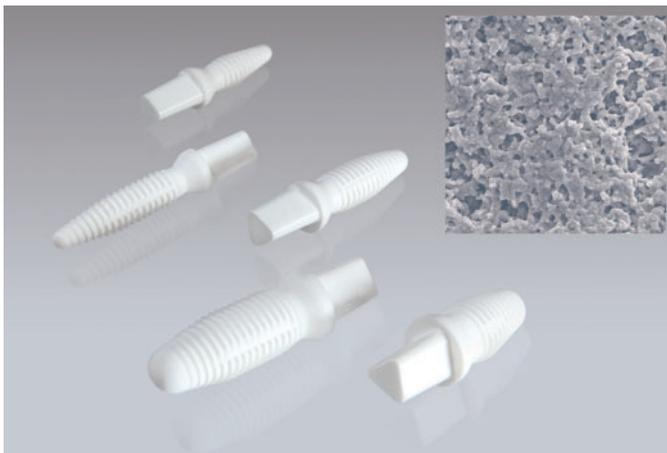


Fig 11 Oral implant made of zirconia ceramic. The Ziraldent®-Implant and ZircaPore®-Surface.

1989	Publication by Rieger ²⁴ on the performance of modern bioceramics
1990	Root posts made of HIP zirconia after Sandhaus
1993	President DCS users discover HIP zirconia for dental CAD/CAM machining
1993	Introduction of HIP zirconia at DCS Dental AG
1994	Wohlwend obtains zirconia as a pre-sintered body for CAD/CAM machining
1995	Market leader in the field of root posts made of HIP zirconia
1998	Abutments start to be made of HIP zirconia by Wohlwend ¹⁰
2000	Market leader with HIP zirconia for CAD/CAM machining
2002	First surgical instruments for oral implantology made of HIP zirconia
2003	First oral implants made of HIP zirconia available on the market
2007	Presentation of the Ziraldent®-Implant with the surface ZircaPore®
2007	Presentation of coloured zirconia CAD/CAM-blanks (HIP and pre-sintered)

Table 2 Milestones of Metoxit AG in the introduction of zirconia into dentistry.

niun base. This meant that the fixing screws did not sit in the zirconia but in a tried and tested titanium system. Today Metoxit AG supplies numerous customers with abutments made from zirconia-TZP-HIP in various configurations, in some cases combined with titanium parts. Clinical studies have reported positive results in this area^{9,12}. Metoxit AG have also been producing surgical instruments for oral implants for the past three years made from Ziraldent, a high-strength composite ceramic. These instruments are particularly characterised by their long service life and smooth running, and offer the advantage of metal-free use. At the same time, the first oral implants made from zirconia ceramic have also been manufactured; these are a focus of current development work (Fig 11 and Table 2)¹³.

The introduction of zirconia ceramic into dental laboratory work took place in the early 1990s when titanium was increasingly being processed for crown and bridge frameworks by means of CAD/CAM technology. This material never achieved any great popularity, which was due to the fact that aesthetics were still poor at the time and the bond strength

Introduction of Zirconia into Dental Laboratory Technology

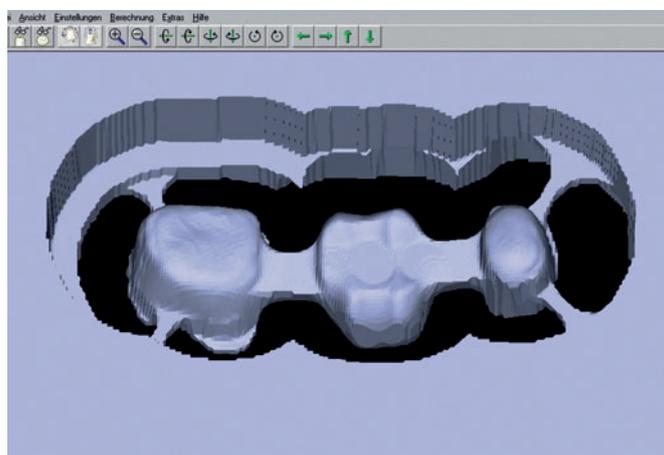


Fig 12 Virtual CAD image of a bridge framework showing the planned milling out of a material blank.

Fig 13 Bridge framework after milling out of a blank made of HIP zirconia ceramic.



Fig 14 Basal view of the ceramic veneered posterior bridge.



Fig 15 All-ceramic posterior bridge inserted into the mouth.



of ceramic to framework was debatable. The desire to use the CAD/CAM systems that had been developed for materials other than titanium led innovative users to the products from Metoxit AG. In 1993, when zirconia was already known in dentistry for post-and-cores, DCS Dental AG (1995–2006 DCS AG, Allschwill, Switzerland; 2006 Bien Air, Biel Switzerland; 2007 withdrawn from the market), Metoxit and the DCS Precident system user Josef Hintersehr were the first to adapt their system to zirconia ceramic^{14,15}. To gain the maximum benefit from the positive material properties of zirconia ceramic for crown and bridge frameworks, the dental technology parts were ground out of zirconia-TZP-HIP blocks using sintered diamond instruments (Figs 12 to 15)¹⁶. As a basic principle, this application has remained the same to the present day. Other companies such as HintELs (Griesheim), newly founded at the time, also went down this route of CAD/CAM ‘zirconia hard machining’³.

The fact that the veneer ceramics for titanium were also suitable for zirconia frameworks, in terms their coefficient of thermal expansion (CTE), was being exploited by the



- ▶ Initial FS–Zr, GC
- ▶ Cercon KISS, Degudent
- ▶ Lava Ceram, 3M Espe
- ▶ Creation Zr, Girrbach
- ▶ Cerabien ZR, Noritake
- ▶ Eris, Ivoclar
- ▶ NobelRondo, Nobel Biocare
- ▶ e.max Ceram, Ivoclar
- ▶ Zirox, Wieland
- ▶ VM 9, Vita Zahnfabrik
- ▶ Sakura Interaction, Elephant
- ▶ Vintage ZR, Shofu
- ▶ Diverse titanium ceramics

Table 3 Current veneer ceramics for frameworks made of zirconia ceramic (some of the product names are registered trademarks of the manufacturers).

mid-1990s. One weakness in this crown and bridge system proved to be the bond between the veneer ceramic and the zirconium framework. This weakness was revealed by analysis of clinical trials and was then resolved by the introduction of special veneer ceramics for zirconia (Table 3). So far there is no common agreement on basic procedures such as the surface treatment of the veneering areas of the framework. Each product of zirconia and veneering ceramic are underlying the individual recommendation of each manufacturer. These recommendations vary significantly among products and are sometimes contradictory¹⁷.

In 1994 Arnold Wohlwend looked for a way to machine zirconia in a state that was not yet fully sintered so that the time required for grinding the HIP-zirconia during CAD/CAM machining could be markedly reduced. This led to the creation of zirconia blanks that could be quickly machined in a chalk-like state using tungsten carbide cutters¹⁶. When using this method, it became necessary to machine out the crown and bridge frameworks from the blocks in an enlarged form to compensate for subsequent sintering shrinkage. This enlargement technique was resolved with the aid of the digital components of milling machines. The first system to take up the idea of pre-sintered body machining and make it a technical and commercial reality was Cercon (Degudent, Hanau). The concept was developed in the Department for Crown and Bridge Prosthodontics, under the direction of Prof P Schäfer of the Zürich Dental Institute and at the ETH Zürich under the direction of Prof L Gauckler. In the pilot study this concept was presented as DCM (direct ceramic machining) and was documented as such in the early clinical trials¹⁸. The patients of this study were recalled, and 5 years of clinical follow-up was presented¹⁹.

Since 1998, numerous companies have brought out other CAD/CAM systems aimed at using high-tech ceramics such as zirconia-TZP as framework materials for dental laboratory technology^{3,20}. Machining of the material in its pre-sintered body phase with subsequent sintering has become increasingly popular, as well as CAD/CAM machining of zirconia-TZP in the HIP state. The first clinical trials with zirconia for crown and bridgework in dentistry emerged in the clinics of Aachen, Göttingen, Zürich, Homburg and Malmö. Regarding the clinical experience with zirconia oxide as a framework material for dental restorations, studies are examining follow-up time periods of 5 years. For the studies looking at 5 years, the ceramic material, the manufacturing system and the veneering materi-



Table 4 Overview of clinical trials from bridge prosthodontics with frameworks made of zirconia ceramic. The work was produced with different systems and material combinations.

System	Bridges		Units		Time (years)	Fracture rate (%)		First named author	Year
	Anterior	Posterior	Three	More		Frame	Veneer		
DCM		22	21	1	1	0	0	Sturzenegger ²⁵	2000
Lava		38	38		1.5	0	2.5	Pospiech ²⁶	2003
Cercon		59	44	15	1	0	3.4	Bornemann ²⁷	2003
Cercon		11	11		<1	0	0	Rinke ²⁸	2003
DCM		58			3.5	0	11	Sailer ¹⁸	2003
DCS	3	17	2	18	2	0	3	von Steyern ²⁹	2005
Lava		20	20		2.6		n=5	Raigrodski ³⁰	2006
DCM		33	27	6	5	97.8	15.2	Sailer ¹⁹	2007
InLab			170	32	4		5	Mörmann ³¹	2007
DCS	15	50	43	22	5		6	Tinschert ³²	2007

al were, at the time, being used in a experimental phase. The evidence and conclusions that can be drawn from these reports are limited. However, all studies have reported that no fracture of a framework has appeared. The evidence of the so-called chipping of the veneering ceramics (cohesive fracture within the veneering) is widely discussed.

Table 4 shows the current status of the clinical trials with regard to crown and bridge prosthodontics involving zirconia frameworks and an individually layered veneer ceramic. Some studies are not reporting any chipping, while some authors are expressing their concerns about the findings concerning this issue. The reasons for these chipping phenomena are still not fully explored^{21,22}. One important area of distinct improvement was the software developments in the CAD/CAM systems for anatomical shaping of frameworks, which enabled the production of a veneering layer of uniform thickness.

CAD/CAM Machining of Zirconia Ceramic in Dental Laboratory Technology

In dental all-ceramic work, zirconia-TZP has recently been introduced for the fabrication of framework structures for single-tooth restorations and bridge assemblies. This material offers advantages over alumina because of its higher strength. The frameworks are conventionally veneered by hand with compatible ceramic materials by the layering/sintering technique. The possibility of fixing the veneered restorations onto the prepared teeth or implant abutments with conventional cements is an advantage for clinical ease-of-use. In using CAD/CAM technology, the frameworks are machined out of blanks of the material, which can be in different states of sintering (Fig 16). In dental laboratory work, the processing is currently carried out in three different degrees of sintering³:

1. Machining the framework contour out of a densely sintered framework material (hardened and tempered by the HIP process) with diamond instruments (usually fully sintered) and water cooling.
2. In pre-sintered (also called semi-sintered or partially sintered) material with diamonds and water cooling.
3. As a pre-sintered body in a chalk-like (porous) state with tungsten carbide cutters without liquid cooling.

Each of these approaches has system-specific advantages and disadvantages. Machining of completely sintered zirconia material requires special machines with high rigidity and



Fig 16 Metoxit AG manufactures material blanks in different configurations to order and as specified by dental companies.

longer grinding times, which means correspondingly high tool consumption. The use of semi-sintered zirconia material can shorten the grinding time and greatly reduce tool consumption. Furthermore, the machining equipment is exposed to far fewer stresses. Machining zirconia ceramic in a less than fully sintered state (groups 2 and 3 above) always requires enlarged shaping of the object, followed by sintering in special furnaces and sintering shrinkage inherent to the system. This method is the most commonly used today in dental laboratory technology.

While products made from zirconia are growing in popularity in dentistry, Metoxit AG is already working on the development and introduction of more generations of oxide ceramics for medicine. In this context, the material called Ziraldent® (alumina toughened zirconia) is a good example of how increased strength, compared to zirconia, has been achieved by the use of industrial manufacturing methods. The manufacturing process requires a HIP treatment in addition to the sintering, and this material can no longer be commercially machined on dental laboratory CAD/CAM systems because of its high strength. It is therefore only suitable for industrial processing, e.g. for surgical instruments, implants and root posts.

Quality assurance is a major concern in industry and especially in the medical technology sector. Metoxit AG was certified in accordance with ISO 9001:1994 in 1997 and ISO 9001:2000 in 2004. For the medical sector, the company is certified in accordance with ISO 13485:2003 and the European directive 93/42/EEC of Appendix II. The extremely high quality assurance standards, which must be met as a matter of course for products used in orthopaedics, have also proved to be a perfect precondition in relation to dental ceramics for ensuring excellent reliability and user safety of the products manufactured.

Metoxit AG has a wealth of expertise in the field of oxide ceramics for medical use. From among this group of materials, zirconia-TZP (especially in the HIP form) has become increasingly attractive for restorative dentistry since the mid-1990s. Despite the relatively short clinical observation phase from the medical point of view, the results so far justify its use, while the long-standing use of zirconia in orthopaedics (successfully employed

[Future High-tech Ceramics](#)

[Quality Assurance in Production](#)

[Discussion](#)



since 1985) serves as an excellent reference. The Swiss company is interested in working with partners from the dental industry, not only to manufacture medical devices in the form of finished parts but also as a supplier of semi-finished parts. Since the company was formed in 1978, Metoxit AG has stuck to this principle of being a supplier without direct distribution to customers, namely dentists and dental technicians. In most cases the consumer has no idea where the material he has used originated from. Some suppliers of high-performance ceramic products name Metoxit AG as a quality source in order to distinguish themselves from other suppliers and as a way of substantiating their competence and product quality. This is particularly important given the events in 2001 when a competitor had to withdraw from the production of ceramic products for medical use because of faulty products. The user and, not least, the patients must be able to rely on standardised quality in the manufacture of ceramic materials and products. The years of development work and the experience gained by Metoxit AG in the field of medical devices are documented in numerous publications²³.

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