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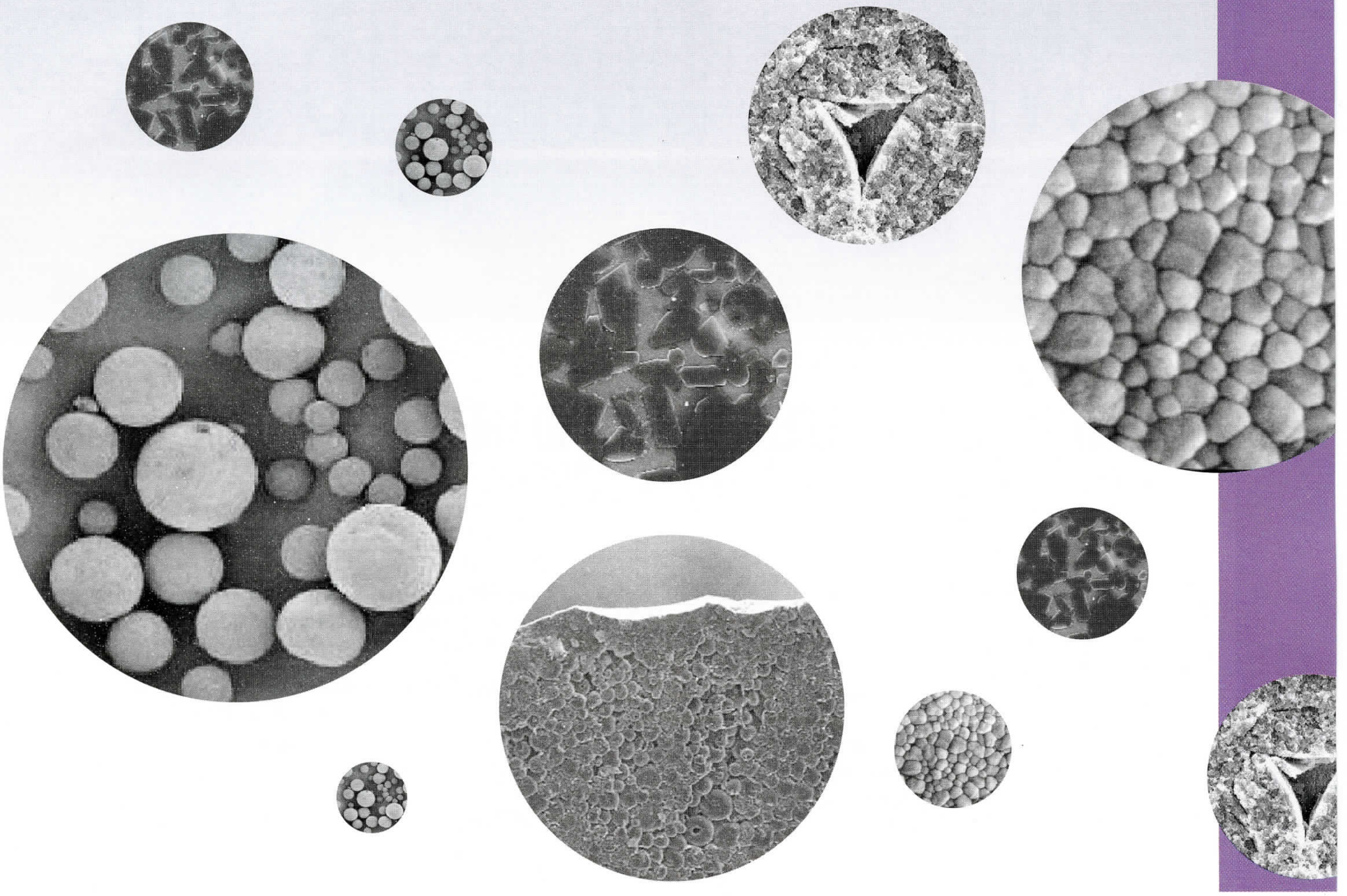
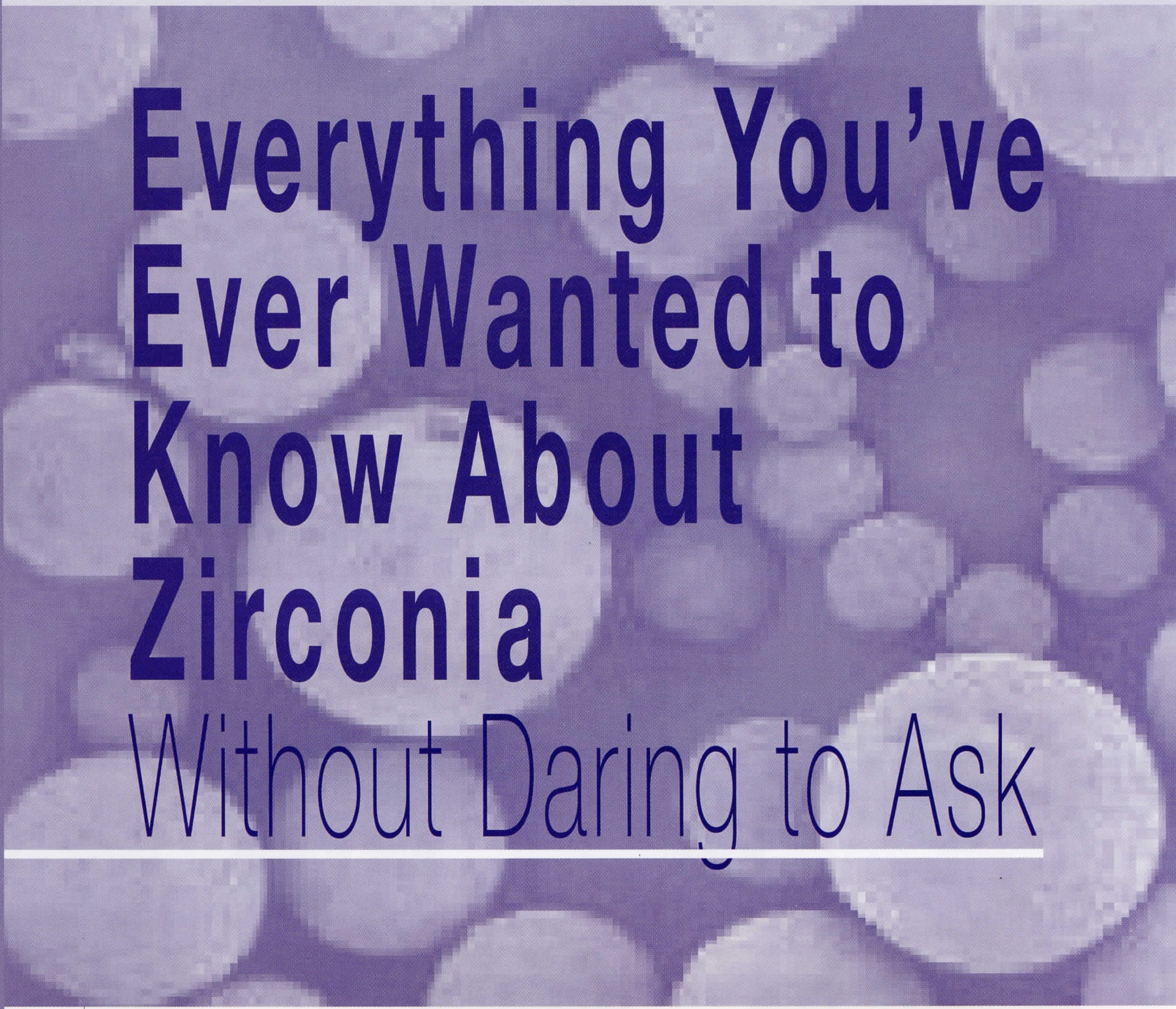
THE TRUTH ABOUT
ZIRCONIA

Even though it was introduced on the dental market around seven years ago, the properties, capacities and limits of zirconia are still poorly understood. There are essential rules that technicians need to respect in order to guarantee a high quality product, and it is sometimes necessary to get rid of certain prejudices based on partially reported or poorly interpreted facts.





Everything You've Ever Wanted to Know About Zirconia

Without Daring to Ask

INTRODUCTION TO CERAMURGY AND THE CLASSIFICATION OF ZIRCONIA:

Let's start with the following definition for a ceramic:

> *"A generally brittle, essentially non-metallic, inorganic material"*

The idea that zirconia is a "brittle material" should be kept in mind throughout the different manufacturing steps for all zirconia products.

This encompasses a large part of the know-how of all manufacturers of ceramic.

Looking at the diagram on the right-hand page "Effort Deformation of a Brittle Material" (S1), you can see the absence of ductility in the ceramic, which is shown by a lack of elasticity.

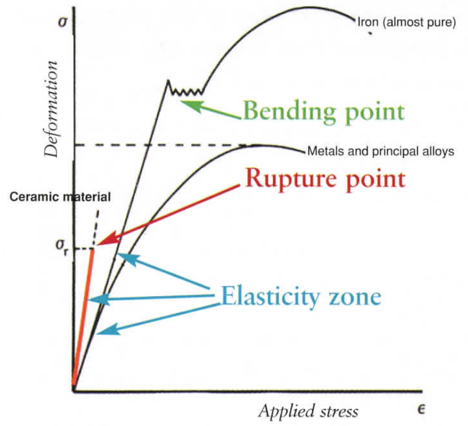
This behaviour plays an important role in the conception and production of zirconia restorations.

The brittleness of zirconia should be integrated into the conception of a product, keeping in mind:

- **The material: the choice of raw materials and the grade of zirconia with respect to its application.**
- **The use: specifications of the product and the environment in which it will be used.**
- **The conception: a product's design adapted to ceramic and to its use. It is impossible to "copy and paste" from a design adapted to metal.**
- **The elaboration: the process of shaping, milling and sintering. It is important to recognise the economic point of view as well as the environment in which the product will be placed and the uses to which it will be subjected.**

Again it is essential during the entire production of a restoration to remember that zirconia is a "brittle material," (especially while designing and milling).

S1 *Effort-deformation of a fragile material*



This graph shows different reactions to applied stress.

Ceramic materials, shown in red, deform elastically and then rupture.

Metals deform similarly, however they bend instead of rupturing.

ZIRCONIA IN ALL OF ITS STATES AND DENOMINATIONS:

First, a reminder of the basics:

- **Zirconium (Zr) is the metallic element that exists in the Earth's crust in great quantities.**
- **Zircon ($ZrSiO_4$) is a chemical compound containing zirconium called Zirconium Orthosilicate, which is very different from zirconia.**
- **Zirconia (ZrO_2) is zirconium dioxide (or oxide), which is translated as "la zircone" in French and "das Zirkon" in German.**

Certain brand names on the dental market make the distinction even more confusing. For example:

- **The brand Zirconia® is, in reality, a ceramic with a porous matrix containing zirconia and alumina infiltrated by a vitreous phase. This makes it chemically very different from zirconia, and its mechanical properties are much lower.**

We will not return to the different crystalline states of zirconia (monoclinic, tetragonal and cubic), but remember that at an ambient temperature, the monoclinic phase is stable.

When the temperature is raised to around 900-1100°C, the volume of zirconia varies as it moves from monoclinic to tetragonal (martensitic transformation).

Because of this important variation in volume (about 5%), it is important to stabilise zirconia at an ambient temperature in the tetragonal phase (called the quadratic phase) for the production of all manufactured products.

Thus we will speak of TZP (Tetragonal zirconia polycrystal).

There are several ways of stabilising zirconia, but for all of these, the addition of a stabiliser should be undertaken in the most uniform way with good atomic distribution:

- Stabilisation can be undertaken with magnesium oxide (also called magnesia (MgO)), or with calcium oxide (commonly called lime (CaO)). These two substances are used principally as stabilisers for the production of industrial parts. The mechanical resistance obtained is generally rather low, around 800 MPa with three point flexion and relatively sustained colouration (deep yellow or cream).
- It can also be achieved using yttrium oxide (Y_2O_3). This is the stabiliser most often used in the ceramic industry for mechanically demanding applications. When 3% (mol) of Y_2O_3 is used, the mechanical resistance achieved is relatively elevated – between 1050 and 1250 MPa with three-point flexion (practically three times higher than for alumina, which is 400 MPa). The toughness K1C (the capacity to resist the formation and propagation of cracks) is eight to ten MPa $\sqrt{m}$, compared to 4 MPa $\sqrt{m}$ for alumina. This is called TZP-3Y or TZP0.
- Cerium oxide (CeO) can also be used as a stabiliser, but it is not as well known. However, its use could be expanded. Its toughness is substantial, reaching 20 MPa $\sqrt{m}$ as long as other mechanical properties, such as flexion, are satisfactory.

Yttrium stabilisation of 3% (mol) is currently most frequently used for mechanical and medical applications. However in order to obtain the most optimum mechanical properties (well stabilised zirconia) with a maximum of the tetragonal phase (metastable phase at an ambient temperature), it is essential to perfectly master and control the final microstructure.

To do this, three essential parameters must be observed and respected:

- The stabilisation rate – for yttrium oxide it is 3% (mol), which is often guaranteed by the manufacturer
- The average size of the crystals after sintering, which should be inferior to the critical size (about 0.6 µm). Above this, destabilisation in the monoclinic phase occurs.
- The optimum density – generally between 6.05 and 6.10 g/cm^3.

Other factors coming from the intrinsic properties of the powders will equally act on the size of the crystals and consequently on the degree of stability:

- The specific surface area of the powder plays a direct role on the reactivity of the crystals and on their behaviour during sintering. This also affects compacting during shaping.
- The granulometric distribution is equally important because an elevated rate of large zirconia grains can diminish the quadratic phase rate.
- Finally, the sintering temperature plays an essential role on the size of the crystal. This step should be undertaken while carefully controlling the parameters of the sintering furnace. An initial validation of these parameters is essential to control the properties of the material. For a single powder, the properties can change between two furnaces, between different brands or between the positions of the parts in the furnace. Maintenance of the parameters is also necessary because they can evolve with time and can include: a change of heating elements in the furnace, the existence of heterogeneity in the interior of the furnace or variations in the control systems.

These factors are never mentioned, yet they are a daily occurrence in the ceramic industry. A lack of validation of these processes (especially the variations: during sintering, for example) can be catastrophic for the behaviour of the material with use and with aging.

Sampling, measures and controls should be applied to parts that have undergone the entire process. Often manufacturers rest on norms that clearly indicate these measurement protocols.

SHAPING ZIRCONIA BLANKS:

In the dental industry, several different types of technology are used to shape zirconia blanks by compacting:

- **Unidirectional pressing (uni axial, see figure S2) creates density heterogeneities in green state zirconia, including different shrinkage. The shape of the blank, however, is very precise.**

This process can be suitable for small blanks destined for single-unit crowns but can present problems for larger pieces destined for bridges.

- **Isostatic pressing or Cold Isostatic Pressing (CIP, see figure S3) assures density homogeneity in un-sintered (green state) zirconia. The shape resulting from this type of pressing is not very precise, necessitating extra milling to obtain a blank. This causes a loss of important material.**

This process allows for the creation of large volume blanks, in which full arches can easily be milled. It also guarantees the homogeneity of the material throughout the entire blank.

- **In order to save production materials, certain manufacturers combine the two processes, using the following chronology:**

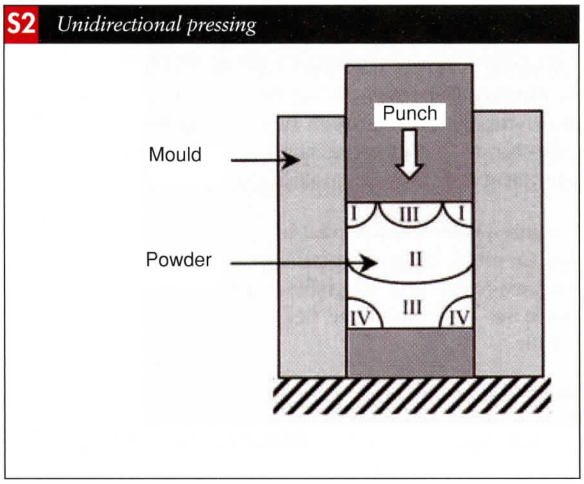
1. *Unidirectional pressing to obtain the shape and avoid losing material*

2. *Isostatic pressing to assure the homogeneity*

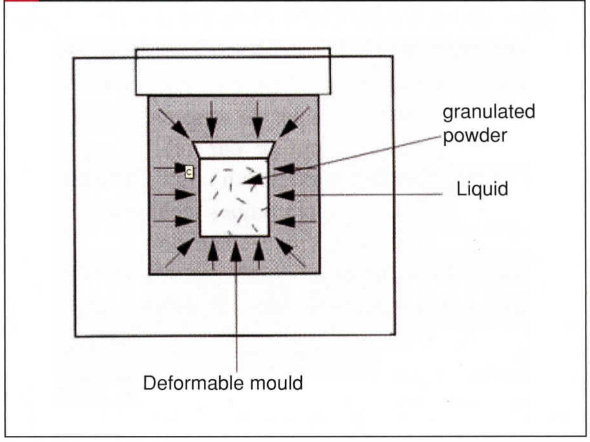
The association of the two techniques creates blanks with regular shapes and homogeneous density from the isostatic pressing. The quality of the material obtained from this system is virtually equivalent to using isostatic pressing only.

In any case, it is rare to hear about the technology used to make blanks. It often remains part of the know-how and secrets of the manufacturers of zirconia.

S2 *Unidirectional pressing*

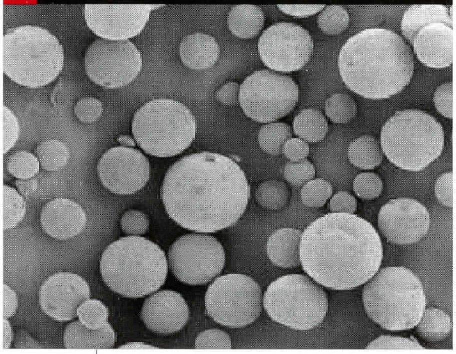


S3 *Cold isostatic pressing*

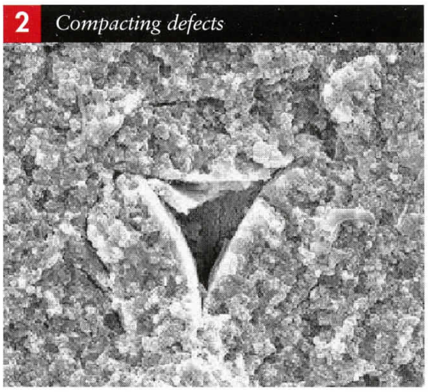


S2: The zones in the corners I and IV are the zones with the highest pressure. Zone III is intermediate and zone II is homogeneous but has the least pressure. A blank made after such a process will have unequal density and, thus, unequal shrinkage after sintering.

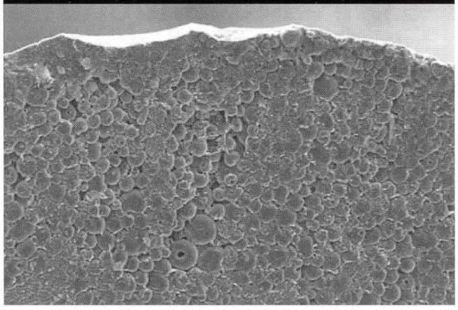
S3: The pressing is uniform.



1 *Atomised zirconia*



2 *Compacting defects*



3 *Residual spheres from atomisation after sintering (photo taken with an electronic microscope)*

THE IMPORTANCE OF THE BASE POWDER:

These different techniques necessitate that zirconia blank manufacturers use yttrium stabilised zirconia "atomised" with dispersants, plasticizers and binders, which appear as tiny balls of about 80 to 150 µm (Fig. 1).

These additives give zirconia good castability and compactibility, and certain binders create overall cohesion of the blank.

A blank made with a low quality "atomised" powder that flows poorly and is prone to deformations will have internal defects. These will remain after pre-sintering and sintering, and will become major areas for fractures.

Using a low quality powder weakens the density and alters the mechanical properties, but, visually, the material has the same appearance as a high quality powder (Figs. 2 and 3).

Thus, it is important to know the origin, the properties and the tracking of zirconia blanks. Do not rely solely on marketing documents, which are often overly optimistic about the performance of products and materials.

GREEN STATE OR PRE-SINTERED?

Today, most CAD/CAM systems on the dental market mill pressed blanks (unidirectional, isostatic or a combination of the two processes) in a pre-sintered state.

Some manufacturers mill green state (un-sintered) blanks.

The two techniques give seemingly equivalent results, although each has its advantages and disadvantages.

The table below illustrates these attributes.
Note: milling time and precision depend on the type of machine used and its characteristics (number of axes, positioning and displacement), as well as the quality and mastery of the tools.

	Milling: Green state	Milling: Pre-sintered
Resistance of blank	Average	Good
Milling time	Very Good	Good
Precision	Good	Good
Use during production	More difficult	Good
Wear of tools	Average	Fast

HIP OR NOT?

Hot Isostatic Pressing (HIP) is an expensive process whereby manufacturers of ceramic use a thermal treatment preferentially after milling and sintering.

The process consists of applying 1000 to 2000 bars of pressure to TZP zirconia while it is brought to a temperature just below that of sintering. Thus we speak of HIP TZP.

It is made only when the use of the product necessitates it – for example, when parts require very large security coefficients (aeronautics, spatial and medical implants). Only precision grinding with a diamond bur (costly) can be made after the thermal treatment in order to guarantee precision to the order of a few microns. This treatment, of course, gives the zirconia even higher mechanical properties: between 1400 and 1600 MPa. This is the result of an increase in density from diminishing internal porosity.

From a strictly economic point of view, it is impossible to reasonably foresee milling into a blank that has been subjected to a HIP treatment.

From a mechanical point of view, TZP zirconia, which has undergone normal sintering (not HIP), suites the majority of dental reconstruction cases. The design of the super structure must be respected, however, by keeping in mind the characteristics of "brittle materials" and the dimensions adapted to the material's properties.

THE PHYSICOCHEMICAL PROPERTIES OF ZIRCONIA:

Very often marketing documents are only based on mechanical resistance in flexion. They rarely explain test conditions, applied norms or even whether the flexion is three points, four points or biaxial.

Yet these three types of flexion for the same zirconia and the same manufacturing process will necessarily give different results because the shapes, the dimensions and the level of preparation of the test samples and the stressed zones are different.

Thus it is essential to know the test conditions before interpreting the results and comparing them to cases in which the conditions were different.

Additionally, as seen above, sintering plays an integral role in obtaining optimum characteristics of zirconia. The fact that sintering conditions may vary from one laboratory to another can also give different results when all other conditions are equal.

Milling green state or pre-sintered zirconia, as we will see further on, can also act on the mechanical properties by introducing defects, splinters and micro cracks.

Non-HIP TZP zirconia stabilised with yttrium (3% (mol)), that is exempt from macro defects inherent in the material (internal porosity) and cracks introduced from milling will have the following characteristics:

Density	6.05 – 6.10	g/cm^3
Resistance (three point flexion)	1050 – 1250	MPa
Resistance (four point flexion)	800 - 1000	MPa
Toughness K1C	6-8	MPa $\sqrt{m}$

Flexion resistance indicated at a greater level – 1600 MPa, for example – is obtained from zirconia that has undergone hot isostatic pressing and not regular sintering.

- Zirconia colouration introduces structural flaws at the atomic scale because of the presence of mineral additions (colorants). Thus it slightly lowers the mechanical properties by around 10 – 15%.

OTHER CHARACTERISTICS NEVER MENTIONED:

There are other characteristics that are almost never mentioned and are important to keep in mind for brittle materials such as zirconia.

THESE INCLUDE, AMONG OTHERS:

- The toughness K1C: capacity to resists cracks. Alumina has a relatively low resistance to cracks (around 4 MPa $\sqrt{m}$), whereas TZP zirconia has twice that amount (8 MPa $\sqrt{m}$).
- The Weibull distribution: this shows the probability of breakage and, thus, the frequency of micro-defects.

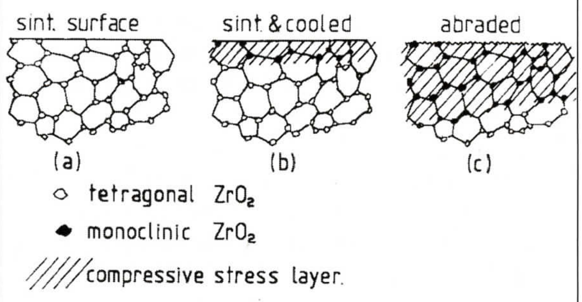
THEY DEPEND DIRECTLY ON:

- The quality of the raw materials (blanks) and their reproducibility
- The control of the machine's parameters (this is difficult when milling by hand)
- The validation of different operations of the manufacturing process
- The monitoring and maintenance of production devices (any loss of precision from the machine, wear of tools, etc...)
- The reliability and reproducibility of the entire manufacturing process

Try not to enter into the "who has the highest mechanical resistance" game, or to:

- Proclaim that zirconia is destabilised when retouched with a diamond bur after sintering. This is true, but only for a thin layer (a couple of microns thick), which has only a very small connection to the product's thickness. Of course it would be best to limit this by milling under water to avoid heating the area.

S4 *Surface destabilisation of TZP*



By far the most important part of retouching is the possible reduction of the dimensions under the recommended limits or the appearance of a micro-crack that cannot be detected visually except under ultra-violet light (Fig. 4).

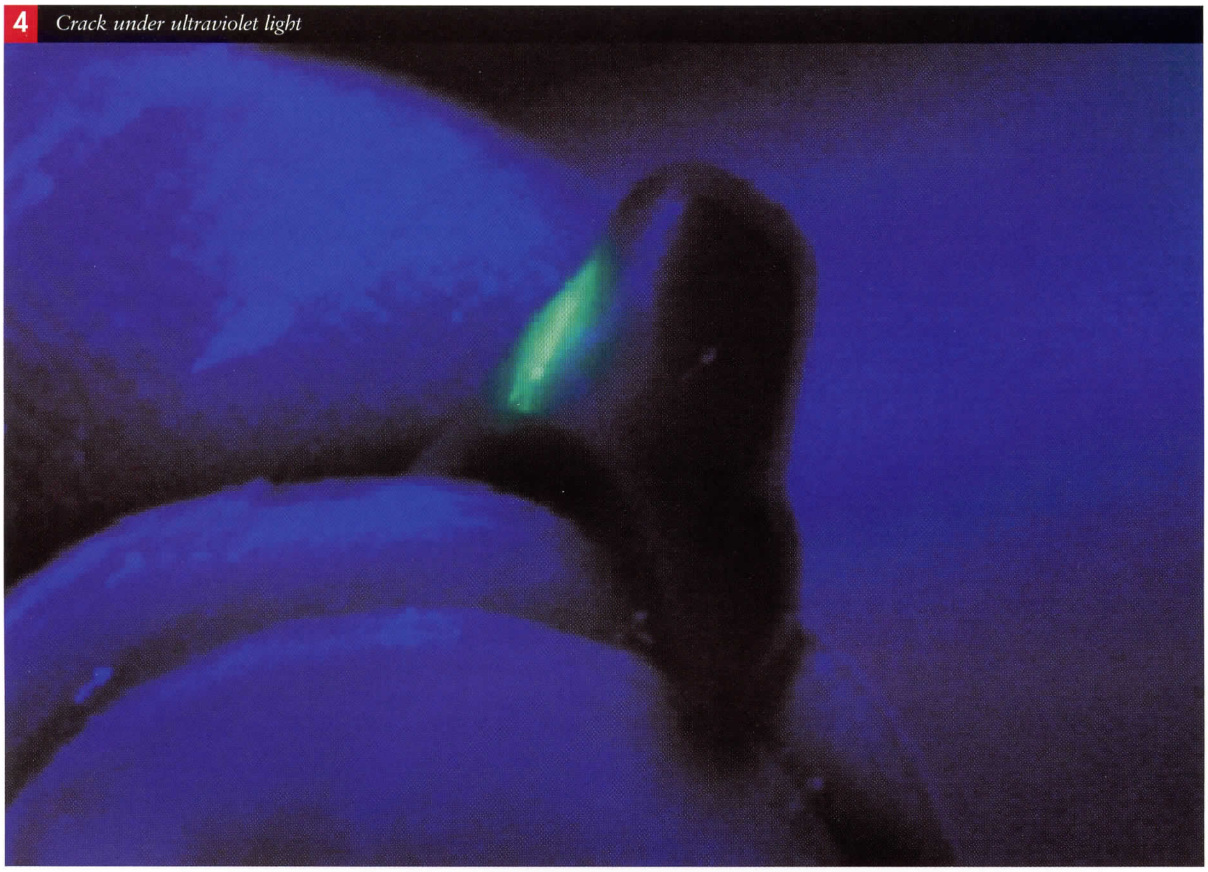
In order to avoid destabilisation, steam treating is not recommended. Destabilisation caused from steam will not appear until after several dozen hours in a humid environment of 140°C – not in the few seconds needed to correct it during processing.

Additionally, certain grades of TZP-3Y are not very sensitive to water vapour (see the section on aging).

It is recommended to systematically heat zirconia to 1000°C after retouching. This is especially essential when a substantial amount of material has been removed, but it can be ignored for minimal retouches. In all cases it is a good precaution to take, although it is not always necessary.

It has been claimed that mechanical properties are altered by hydrofluoric acid. However, the almost complete absence of a vitreous phase at the joints of the grains makes it very resistant to acid corrosion for relatively short periods of time (24 hours, for example). Of course it is preferable to avoid such a treatment.

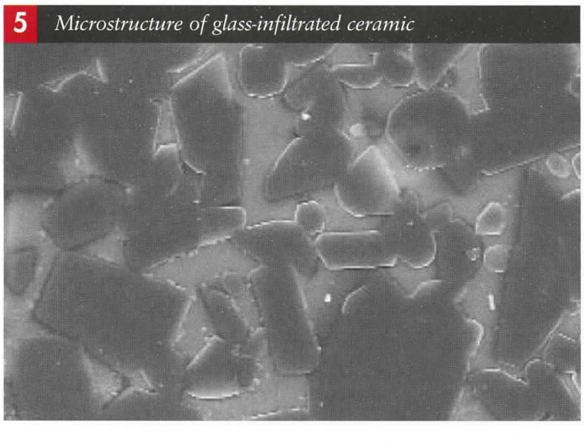
4 *Crack under ultraviolet light*



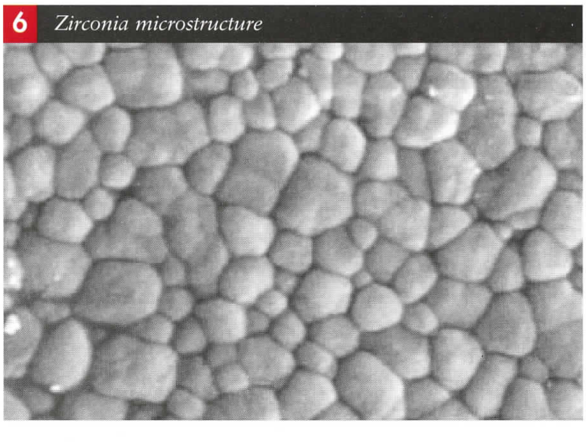
CHEMICAL SOLUBILITY:

We can continue directly from zirconia's behaviour in acid to its chemical solubility. From the almost total absence of vitreous phase at the joint of the grains, TZP zirconia has very limited solubility when compared with other types of ceramic, such as Empress or Inceram, (Figs. 5 and 6). These contain significant proportions of vitreous phases, favouring the solubility of the materials. Tests are led conforming to norms (ISO 6872; <2000µg / cm^3).

5 *Microstructure of glass-infiltrated ceramic*



6 *Zirconia microstructure*



THE INFLUENCE OF DESIGN AND MILLING ON MECHANICAL PROPERTIES:

Assuming that the material (blanks) is exempt from defects and that the sintering is mastered and validated (giving optimum mechanical properties and guaranteeing a quality micro-structure in order to obtain TZP), operations that will significantly influence the mechanical properties of the products are:

- **The design of the restoration.** It is essential to adjust designs to the ceramic while avoiding sharp angles where stress is concentrated. The material's minimal thickness should be calculated with respect to the properties of TZP.

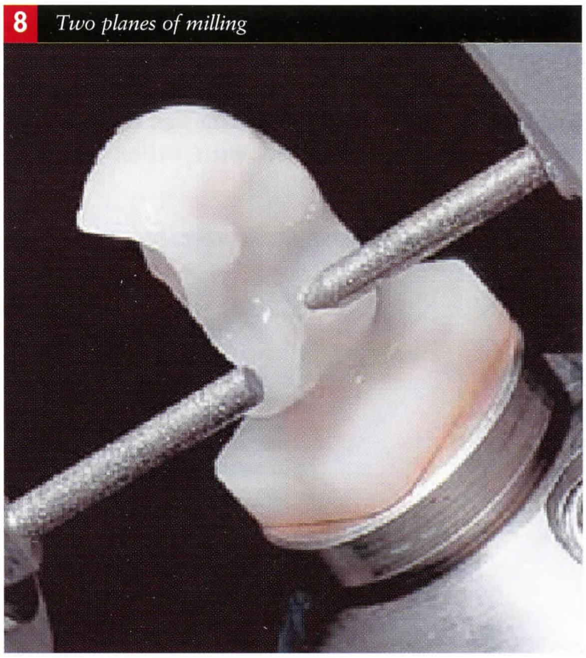
- **The machine's parameters and milling conditions.** A five-axis industrial machine, for example, simultaneously equipped with diverse tools (Fig. 7) will mill the model reliably and precisely, respecting the shapes and dimensions. However a three or four axis machine that can only mill in two planes will only mill a close approximate of the model's shape (Fig. 8).

The quality of the tools and the mastery of their replacement will avoid micro-defects like those shown in figure nine, which appear in both green state and pre-sintered zirconia.

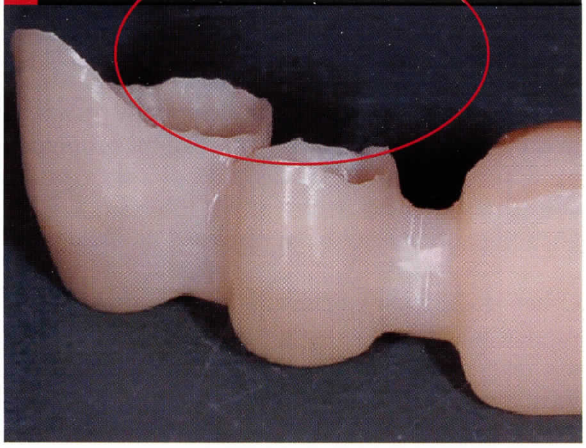
The reproducibility of the cutting conditions (the rotation and advancing speed) as well as shape adapted milling strategies will assure milling precision, especially with respect to fitting and the quality of the margins (lack of breakage). In the end, these precautions will insure that users avoid

7 *Milling machine with five axes (18 or more tools)*

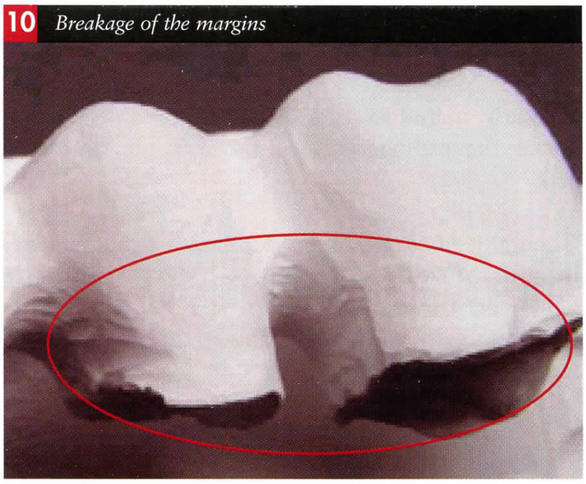
8 *Two planes of milling*



9 *Bridge after sintering*



10 *Breakage of the margins*



the creation of micro-defects and cracks undetectable to the eye, which can later create fractures.

These different parameters are difficult to master with manual milling machines (Fig. 10) and demand a perfect command of the process, which is often difficult to obtain, especially under less-than-ideal economic conditions.

BIOCOMPATIBILITY:

Yttrium stabilised TZP-3Y zirconia's perfect biocompatibility and bio-integration have already been proven in medical applications such as hip replacements, where the material functions with soft tissue as well as with bone.

However each manufacturer of components in zirconia should measure the biocompatibility, since operations in the manufacturing process could render it non-biocompatible.

Likewise, we could ask why it would be necessary to prove biocompatibility when milling a pre-sintered, yet still porous, blank if it is in contact with a non-biocompatible component during milling that would remain after sintering.

This question, of course, is irrelevant when milling sintered blanks.

Norms for such tests are foreseen for this purpose, and European directive 93/42/CEE relating to medical devices demands that these be followed.

As a general rule we can say that yttrium stabilised zirconia is biocompatible, but manufacturers should prove that their manufacturing process results in this biocompatibility.

In the mouth, soft tissue tolerance is comparatively high (compared to titanium, for example), favouring the joining and the cell proliferation of fibroblasts and osteoblasts.

After two years, the marginal tissue is more stable around TZP zirconia than it is around titanium (Bianchi and Coll, International Journal of Oral and Maxillofacial Implants, 2002).

RADIOACTIVITY:

Similarly, manufacturers should supply information about the radioactivity of the zirconia that they sell.

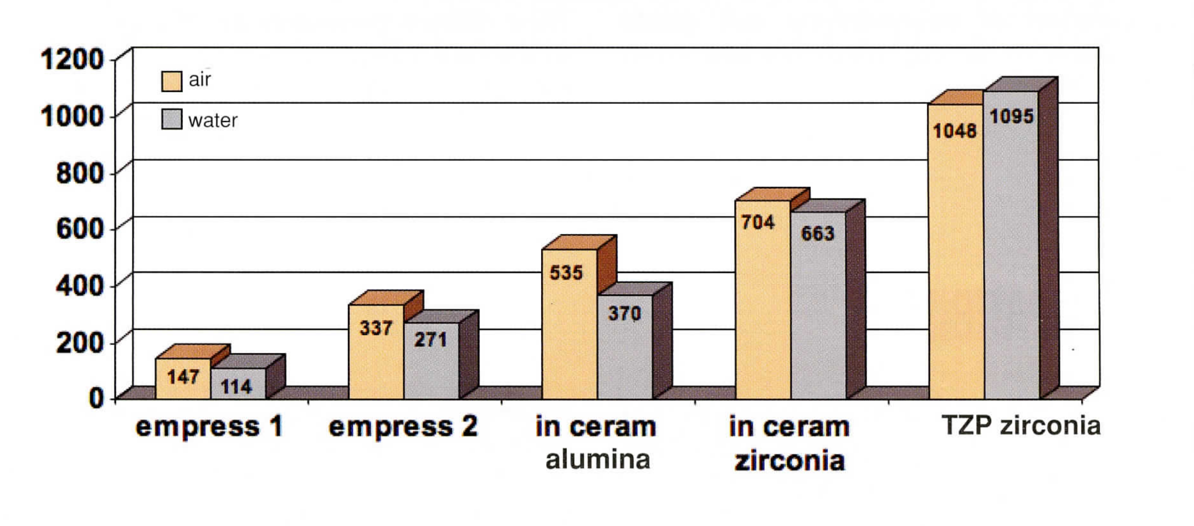
Generally, yttrium-stabilised zirconia's radioactivity is substantially less than what is minimally accepted (norm ISO 6872: 0.2 Bq/gr). This radioactivity is principally due to the presence of hafnium traces in the raw ore.

AGING:

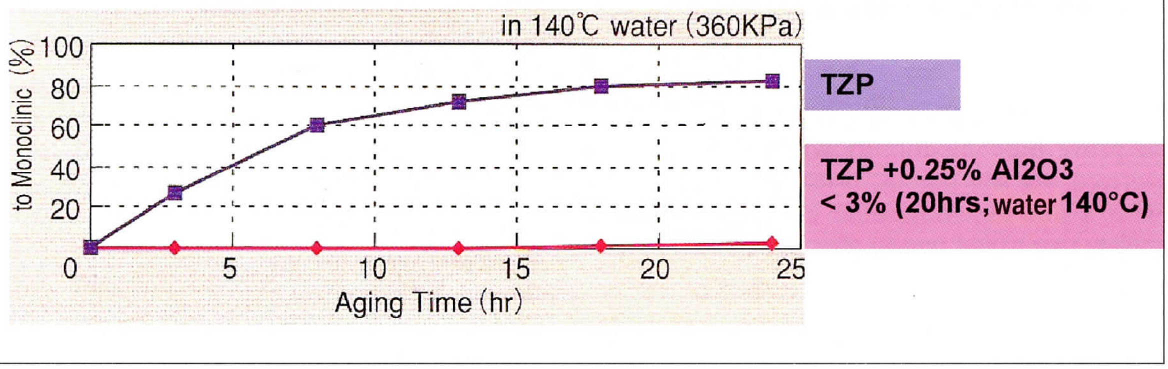
A study undertaken by Sorensen (see table I) shows that soaking ceramic with vitreous phases in water for a week lowers the mechanical properties by deteriorating these vitreous phases (this is connected to the problem of solubility). This phenomenon has not been observed in zirconia.

Other studies have been undertaken using water vapour in autoclaves at a temperature of 134°C without noticeably changing the mechanical resistance of the zirconia.

I *Aging of dental ceramics*



II *Aging of TZP zirconia*



It must be noted, however, that in the past TZP zirconia showed aging under hydrothermal conditions.

Today most parameters that affect aging have been explained.

The aging of TZP zirconia caused by the transformation from tetragonal to monoclinic phases is accelerated by:

- **A temperature between 200°C and 300°C**
- **Water or water vapour**
- **An enlargement of the size of the grains (from the severity of the sintering)**
- **A decrease in the stabilisation rate**
- **Internal constraints**

For a few years now, manufacturers have proposed a powder grade of zirconia for TZP containing a small amount of alumina (about 0.25%), which reduces this transformation and thus curbs aging (see table II). Users should check the grade of powder in their laboratories to verify the material.

IS IT POSSIBLE TO SOLDER ZIRCONIA?

Some have said that it is possible to solder zirconia.

However, when making a restoration in TZP zirconia, constant concerns are:

- **Obtaining a homogeneous product that will guarantee the same mechanical characteristics throughout its volume**
- **Adapting the shapes and dimensions to the properties of the milled material**
- **Sintering the product in optimum conditions in order to achieve maximum mechanical properties**

THE NEXT THING YOU KNOW, WE ARE LED TO BELIEVE THAT ZIRCONIA CAN BE SOLDERED WITH A PRODUCT WHOSE SINTERING TEMPERATURE IS BETWEEN 680°C AND 1000°C - ALL WHILE KEEPING THE SAME CHARACTERISTCS.

If ceramic is made with a product containing vitreous phases (vitroceramic), elevating the temperature will melt this ceramic where it is in contact with zirconia, binding the surface and eventually penetrating the pores of pre-sintered blanks.

The diffusion of the vitreous phase into zirconia at the atomic level remains to be proven. We can also imagine that mechanical properties (flexion, resistance, Weibull distribution...), which have yet to be recorded, are probably inferior to those of zirconia. Moreover, this material is used at the level of joints, and thus, in the areas that are called upon mechanically.

Finally it is erroneous to think that it will improve the surface state by filling in micro-cracks. If a micro-crack appears, it will never close, and, on the contrary, will increase with corrosion and heat.

CONCLUSION :

TZP zirconia has a bright future in the dental industry and in implantology, but the material must be approached with care.

It is essential to respect the implementation conditions, avoid problems connected to the transformation of the material and watch for any changes in the manufacturing process, which could prove fatal to its reputation.

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About the Author

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After finishing his baccalaureate in mathematics and technology, Gilles Arnaud began his studies in engineering.

In 1984 he received his engineering degree from the French National School of Industrial Ceramic in Limoges.

For more than ten years, he worked for the French Technical Ceramic Society, where he sold zirconia and alumina prosthetic hips to companies in the United States and in Europe.

In 1996, he founded Diatomic – a company working to develop CAD/CAM technology for the dental industry. Notably, he specialised in the creation of zirconia blanks using isostatic pressing for milling zirconia substructures. He focused on ceramic industrial products and the associated manufacturing processes.

He has been an advising engineer since 2007.