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GETTING HOOKED ON ZIRCONIA



About the Author



Richard FOUQUIER Dental Technician

Richard Fouquier was born on the 29th of April, 1956 near Paris. After completing his high school diploma in science, he began a Diploma of General University Studies in chemical physics and became interested in dental technology. In 1978 he obtained his Professional Certificate and has continued to deepen his knowledge, earning a Masters in Dental Technology in 1982, a Degree in Dental Technologies in 1997 and a Maxillofacial University Diploma in 1997.

He divides his time between training courses and conferences, was a final candidate for the contest "One of the best technicians in France" in 2000 and is also the vice-president of the French Club of Dental Ceramics.

Richard Fouquier directed various laboratories in France before moving to the United States to work for a prosthodontic office in Portland, Maine from 2000 to 2003. There he had the opportunity to be in direct contact with his patients.

Since then, Richard has returned to France where, in 2004, he created the RVF Laboratory.

ADOPTING A NEW METHOD

It is clear that zirconia is going to become more frequently used in our profession, and therefore, specific new practices will have to be incorporated into our daily routines.

But how do you adopt a new material if you are not familiar with it or how to use it?

Over the years, PFM technology has become more reliable - improved to the point that there are very few problems left. However, the same distrust we had for PFM in the beginning we now hold for

porcelain fused to ceramic. One will surely come across problems if the same method used for working PFM is used to process zirconia. This will lead to criticism, causing the condemnation of the material if left unchecked.

Therefore, understanding the material from a chemical and physical point of view is the first step to mastering it.

Afterward, it will be possible to return to the fundamental principles that bind the two materials together.

A BRIEF HISTORY OF ZIRCONIA

After noticing that zirconium and its oxide crystallize with substantial stability, high resistance and finesse, chemists decided to transform it into an artificial diamond, destined to be used as a tool for the dental industry (for cutting, grinding, etc...).

Its high mechanical and thermal resistance led manufacturers to add it to traditional glass in order to obtain materials that have similar properties, such as Pyrex.

Afterward, these same properties were taken advantage of in fields like aeronautics, in which thermal shields for the Apollo space caps were made to protect the equipment upon re-entry into the atmosphere.

Medical surgery has similarly become interested in the material for these reasons, as well as for its biocompatibility. However, problems with weakening arose after poor milling and impeded further development.

By extension, dental implant surgery has also become involved with zirconia for its mechanical properties, for its biocompatibility and also for its optical properties.

Unfortunately the problems encountered in medical surgery have somewhat cooled the enthusiasm for it in the implant industry.

At the same time, the restorative dental industry was interested in ceramic substructures as an alternative to metal frameworks for their optical and mechanical properties, even though digital milling technology was still developing.

This is how zirconia has progressively made its entrance into our laboratories.



THE MATERIAL: ZIRCONIA

Zirconium, number 40 on the Periodic Table of Elements according to Mendeleev, can be chemically considered as a metal.

As a pure, non-composite element without vitreous mass, it is made up of very small crystals called "crystallites," which are three times smaller than iron. Though very hard, it can be finer and smoother than steel. Since consumes almost no oxygen, it is resistant to oxidization, even when submitted to common oxidizing agents.

In order to use zirconium, which is too stable in its natural state, one is forced to industrially process it at very high temperatures to arrive at oxidation, which will make it easier to combine.



This is how one obtains the white powder called zirconia.

Zirconia, the oxide of zirconium, also has a regular structure and a high level of stability, leaving little room for possible impurities. Certain temperatures, however, can be detrimental to zirconia.

THE CHEMICAL MAKE-UP OF ZIRCONIA

Like in its metallic state, the electronic energy of zirconium oxide participates in its own crystalline cohesion, indicating the existence of electric conductivity, electromagnetism and the possibility of polarity in any piece made from the material, mostly with magnesium stabilised zirconia.

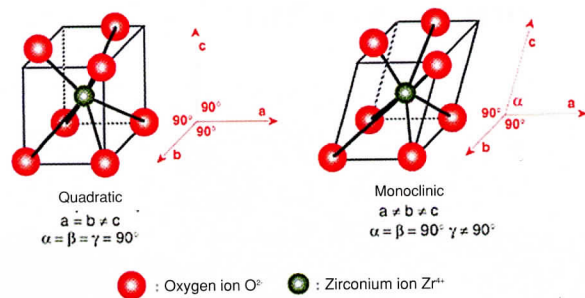
However, it is all a question of balance. The fact that there are small structural crystals, which are beneficially homogeneous for solidity, brings about electronic diffusion of a small magnitude, producing less retentive surface energy (Van der Waals Force).

In addition, zirconia consumes its own energy to

transform itself, and removing any would leave it fragile. Therefore, work protocol must preserve these properties and not spoil its electronic and energetic potential.

Remember that zirconia is a solid material and is subject to weakening.

DIAGRAMS OF QUADRATIC AND MONOCLINIC CRYSTALLINE STRUCTURES



GOODBYE, CHEMICAL BONDS?

Consequently, in order to create reliable porcelain build-ups on zirconia, chemical and micro-mechanical bonds cannot be counted on.

- not with surface oxidation (which is only possible during industrial processing)
- nor with Van Der Waals Force, which is too weak

However, we can take advantage of two remaining phenomena:

First, we can use the difference of the coefficient of thermal expansion (CTE) between the zirconia and the porcelain, which "sinters" on the framework. This will provide retentive compression, while not provoking any excessive internal constraints or tensions. Second, the adherence of the materials can also be exploited.

HELLO, ADHERENCE!

We can undertake a simple experiment to show this adherence.

When you layer together two plates of glass that are perfectly adapted to one another, it is very difficult to separate the surfaces by tearing them apart. Sliding them apart can also be very difficult if there is no air between them.

However, if the two plates are not perfectly adapted to each other, all you have to do is use water to make them inseparable. In this case it can no longer be classified as adherence, but rather as "pasting" together, since a foreign material has filled the spaces.

Because of electronic diffusion, * closely bringing together the surfaces of two bodies at a distance usually inferior or equal to 10^{-6} Angstroms ** (10^{-6} = one millionth) produces a bond that can be rather strong depending on the state of the surface, the size of the objects and the spaces resulting from the shapes of the two materials.

* Capacity of a molecule's electrons to "explore" a neighbouring molecule, establishing a bond

** one angstrom = 1.0×10^{-10} metres

This adherence is known under the name of welding in dental technology. With a preliminary rubbing, you can increase the electronic surface diffusion, actually intensifying the electromagnetic phenomenon for a longer period of time.

In this way, we can create a magnetic bond of less than 10^{-6} Angstroms, depending on the material selected.

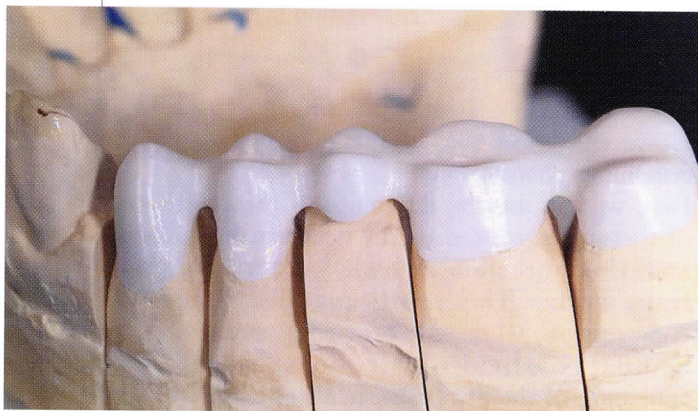
WELDING AND SOLDERING

Connecting two smooth surfaces of the same constitution, without using a third substance is what is called "welding" in dental technology. It is optimal on a smooth-polished surface.

Using a (liquid) fusing material to bind two differently shaped parts is known as "soldering" in dental technology. This process is optimal on a rough surface, which gives a larger surface area for bonding.

ZIRCONIA: A MORE INTIMATE LOOK AT ADHERENCE

It is important to know that in the case of Zirconia, electronic diffusion according to Van Der Waals Force is too weak.



Actually, the natural electromagnetism of the material decreases the distance of rogue "explorer" electrons that are in a simple trajectory at the surface of the solid, rotating counter-clockwise. It acts as additional surface magnetic currents, called "Foucault currents."

These currents are very strong but well under the usual 10^{-6} Angstroms. They are not very active with regard to the surrounding material unless it is fairly close by. In order to take advantage of them, search for the closest distance possible, well below 10^{-6} Angstroms.

There is no vitreous phase in zirconia, but there is in porcelain. This is a material that enables good flow of the composite masses of vitro-ceramics.

Vitro-ceramics have significant vitreous phases. When they are reinforced with Lucite, they are less transparent and have a higher fusing capacity. When the vitreous mass possesses less Lucite, the ceramic is more transparent and has a lower fusion rate, but it is also more brittle.

Therefore this very fluid vitreous mass will play the role of water between the plates of glass in the experiment described above. If it flows well, the intimacy with zirconia will then be optimized, especially if it is reinforced with Lucite, wherein the particles move closer together and take advantage of Foucault currents.

ON THE SURFACE OF ZIRCONIA

It is difficult to visually assess zirconia if the surface state is well done, since much of the roughness is very small - even up to the crystalline scale of the material.

Additionally, the crystals must be completely incorporated on the surface and not separated from the principal mass.

In the absence of the contribution of energy that generates the electronic diffusion, repairing intermolecular links, the slightest separation can become permanent.

Luckily, in the case of superficial breakage, zirconia changes its ordered crystalline structure into a deformed crystalline structure, which is more voluminous and capable of filling small spaces and micro cracks. However, a contribution of energy is necessary to modify its structure and change its physical properties.

A spreading crack generates sufficient energy to change the crystalline structure and is enough for its own repairation. However this property has its limitations.

However, this flow will depend on the temperature:

A compromise would be to find good quality ceramic with a high proportion of vitreous phase, having optimal firing temperature, translucency and stability (constancy) throughout firing. All this should take place under appropriate protocol for preparing the surface of zirconia.

In fact, no matter what protocol was used during its firing, the ceramic added for the build-up will be combined according to its vitreous phase and that of the first coat applied on the surface of the zirconia.

If this initial surface is poorly prepared or altered, the vitreous combination will serve no purpose and can only lead to a separation of the materials.

Fatigue cracks (without energy contribution) can still occur in time. Therefore it is best to spare zirconia from excess stress.

TRIMMING AND GRINDING

Poorly measured trimming can provoke cracks, cracks and straining. Admittedly, this is partially compensated with the energy caused by grinding.

Controlled rotation can create a balance between destruction and preservation of zirconia's properties.

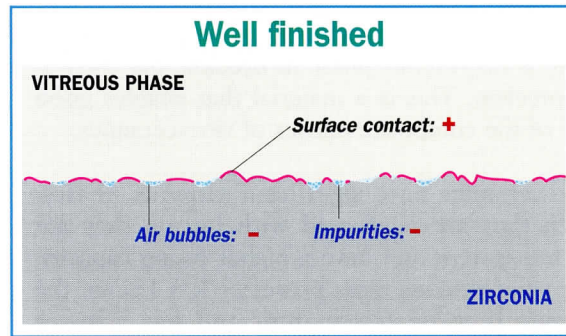
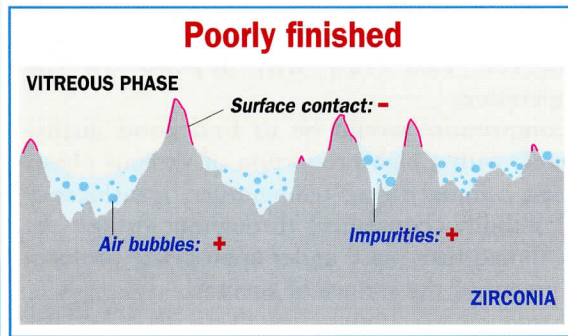
Grinding at a high speed may feel as if it is more effective, but it is much too violent for zirconia.

Adding water would seem to allow working without risks, but that is also an illusion.

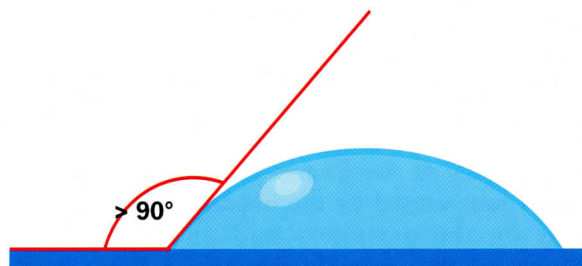
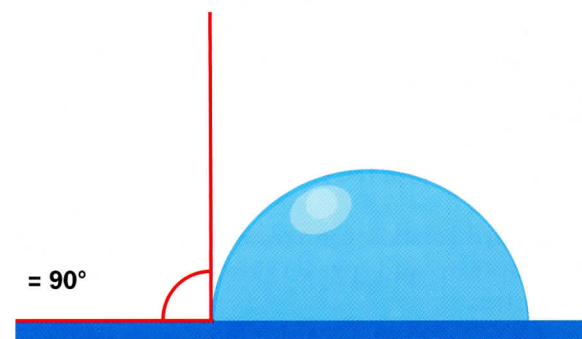
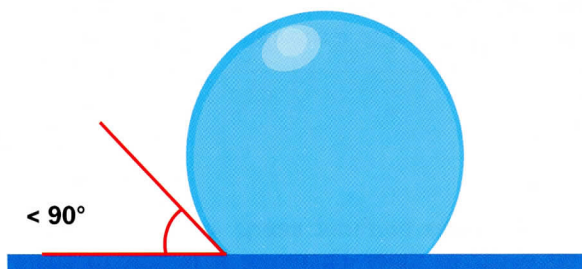
Yes, working in an aqueous medium prevents the propagation of shockwaves and partially absorbs excess heat caused by the impact of the bur, but only on the periphery and on the surface. However, the invisible damage is there, well beyond the periphery.

SURFACE STATE

Being too eager to succeed can cause failure



DISPERSAL



This is a material's ability to allow the dispersal of a liquid on its surface.

It is measured and defined by the angle created between a drop of water and the surface itself, as shown in the figure to the left.

- < 90°: low dispersal
- = 90°: normal dispersal
- > 90°: high dispersal

Causes of low dispersal

- Surface is too rough
- Surface has negative tension (ion-)
- Surface is greasy or dirty

Causes of high dispersal

- Surface is smooth and polished (with low magnetism)
- Surface has slight positive tension (ion+)
- Surface is clean

Normal rotational speed (18-25,000 trs) makes burs and grindstones bounce, using them without truly attacking the surface of the zirconia.

It is nevertheless destructive aggression on the surface, which, luckily, does not have any negative effects on the internal structure. Such speeds are just acceptable for certain stages of polishing.

With adequate tools, speeds of 3 to 12,000 (sometimes 6 to 8,000) are very effective, causing no significant damage to the zirconia. However, to avoid wasting time, be sure not to overheat the piece that you are working on.

If the tools rotate too quickly and the piece overheats, the energy contribution will be too great on the surface and will raise the intensity of Foucault currents, exacerbating the polarity. This in turn will reduce the ability of the surface to disperse liquid, which is necessary to successfully apply porcelain (see diagram).

Thus, it is better to grind after pre-sintering instead of after a thermal treatment.

The less you drill sintered zirconia, the better off it will be!

It is why the industry is turning toward working with green-state (not pre-sintered) zirconia.

IDEAL SURFACE STATE

On the other hand, trimming has to create a sufficient amount of roughness to increase the contact area of the zirconia and the porcelain.

Caution: a surface that is too rough can lead to gorges that are too deep and inaccessible to flow, which can trap gas, air and impurities. These can evolve, pollute or pass through the porcelain during sintering (see diagram).

Additionally, if the surface is too rough it can prevent contact at the bottom of these zones, reducing adherence, which therefore weakens the bonds. This can be detrimental to Foucault currents, creating a double problem: poor retention and “surprises” in the ceramic.

GRINDING TOOLS

Grindstone binder has to be very special: neutral, without oxide, grease, glue or any other component that needs aggressive cleaning after use. This explains the high cost of the tools specifically designed for working with zirconia.

SANDBLASTING AND CLEANING

Zirconia can and must be sandblasted using aluminium oxide (Al_2O_3 , 50 μm , 2 to 4 bars of pressure, 1 cm from the nozzle). This will remove loose crystalline elements and give it a satiny finish.

However, never use scalding liquid to clean zirconia or allow it to undergo an ultrasound.

An ultrasound produces a bombardment of micro-bubbles at close to 1000 meters/s. Admittedly, it is a microscopic distance, but it has a significant impact, which can provoke micro-cracks in the zirconia without any real energy contribution. This could cause numerous fractures.

NEVER USE ULTRASOUNDS, EVEN FOR TATAR REMOVAL

A sensible thermal treatment, however, will burn off impurities on the surface as well as contribute energy, repairing small surface imperfections from grinding.

LINERS

Often, when a coloured binder or liner is applied, it is the first real cause of accidents, and manufacturers are using it less and less.

Since they do not have a significant vitreous stage, their flow is limited. Additionally, the retraction of these materials during dehydration causes them to peel off even after careful application, use of a glass spatula or vibration.

Liners are like shells around the frameworks, and there is little chance that they will hold for very long.

One solution would be to dehydrate the liner very slowly (24 hours), or, even better, not to use one at all.

ZR POWDER

COEFFICIENT OF THERMAL EXPANSION (CTE)

Even if porcelain destined for titanium has been successfully used on zirconia, it is necessary to adjust the coefficient of thermal expansion for zirconia.

Both high and low melting points are proposed, but controlling the CTE for high melting points is difficult and unstable. It is better with a low melting point, but these ceramics are very fragile.

On the other hand, for higher melting points, temperature that would normally not be advised for zirconia is recommended. That being, for such ceramics, it is no longer the contribution of calories in relation to the mass during sintering that raises the temperature (cooler but longer).

A lower melting point allows technicians to better respect the materials. They are better controlled in terms of CTE, but are fragile and cannot tolerate as much repeated sintering, since they lose volume (retraction) and translucence.

Of course there are better zirconium powders than others, beyond personal comfort or the brand names that we are accustomed to. It is essential to try different ones in order to find the most reliable.

A CTE that is poorly handled by manufacturers or poorly used generates weak resistance to effort and strain. Within a short period, the ceramic will break in situ.

COSMETIC STRAIN

Weak CTE causes internal tensions that are characterized by cosmetic fracture lines. These tensions increase with occlusion, spreading to the ends of micro-cracks and transforming them into fractures.

A CTE that is too high will produce a loose ceramic mass, lacking compression around the coping. By itself, it will take all the occlusional force without really sharing with its support. The weak connection with the coping will break, and it will detach like the shell of an egg.

THE SHADE OF ZIRCONIA

Certain zirconia colouration seems to alter surface performance, as well as external CTE.

Darker zirconia shades seem to be the source of worry, even though those obtained by surface saturation are acceptable, since they seem to increase the solidity of the saturated zones.

TOOLS FOR ZIRCONIA

It is essential to have tools (furnace, spatulas, plates, baking supports...) that are reliable and entirely designed for zirconia. These should remain clean, lack oxide contamination and not be used for porcelain powders.

Therefore, invest in a quality furnace for zirconia.



CONCLUSION :

Zirconia can create excellent cosmetic results, and porcelain can be very difficult to remove from a coping if the material is well understood and applied.

The major doubts and concerns with it, like in the past with other products, are created out of ignorance, incomprehension, poor practice and (even worse) the application of practices destined for other materials.

Once these obstacles are surmounted, trust returns along with almost perfectly reliable results. It is essential to find a balance between the

material, personal habits, powders and protocol. Experience makes the difference.

Faced with the incapacity of some to work with zirconia, we cannot give in to their accusations that it is a poor material. With good practices, we can even use acrylic!

So grab your spatulas and brushes!

We will study these phenomena through real tests in another article.