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Dr. Filipe Silva is a professor in the Mechanical Engineering department of the University of Minho, Guimarães, Portugal, and holds a M.Sc. and Ph.D. in Mechanical Engineering from the same university. He has worked for several jewelry companies and has published many papers for journals and conferences.

High-tech ceramics (HTC) are becoming common in jewelry pieces. It comes from their exceptional properties that are noble in terms of mechanical properties, corrosion, aesthetical, among others. Although these materials are considered to be difficult to deal with, mainly processing, sintering, machining, polishing, etc, there are some steps that may allow it to be used by a common jeweller in it's bench. This paper will present the steps that are common in the processing of high-tech ceramics manily, ZrO₂ based ceramics. Sinthesys, mixing, coloring, pré-sintering, machining using computer numerical control (CNC) millers and/or manual machining (files, drills, etc.), final sintering and polishing. The importance of some parameters that are relevant on processing of these materials will be presented. It will present the main challenges and provide information about how to deal with the difficulties to process such materials. Examples of final components will be shown. A few considerations on design of jewelry components that contain high tech ceramics along with gold will also be presented.

“High-Tech ceramics on jewellery: processing and applications”

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1. INTRODUCTION

Throughout the last years, a trend to incorporate new and unusual materials in the manufacturing of jewelry items has been seen. Wood and ceramics are two good examples of that. The employment of high strength ceramics have started a few years ago mainly in watch industry, with Rado® standing out as the best example of differentiation by the type of materials used to manufacture their watches. Materials like zirconium oxide, titanium oxide, tungsten carbide, aluminum-oxide, lanthanum, and nanocrystalline diamond have been used to that end. With a few years of delay, the jewelry industry has awaked for this new trend and started to take advantage of the benefits of the so-called high-tech ceramics. In fact, they have several attributes that provides them a great appeal to be used in jewelry items, such as: high strength and fracture toughness; high hardness and wear resistance; good chemical resistance; they don't tarnish; the material can be colored, and the color doesn't fade. The extreme heat applied in the manufacturing process is perhaps the major limitation of these materials. To date, it is possible to find jewelry items encompassing high-tech ceramic components in brands like Bulgari®, Chanel®, Baraka®, just to mention a few.

Among the ceramics used in the production of jewelry, the zirconium oxide (zirconia) is probably the most used so far. Sitting on the shoulders of technology used in prosthetic dentistry, product suppliers like Zirkonzahn have turned available the technology produce colored zirconia items from CAD/CAM systems (Figure 1) out of machinable colored zirconia blanks (Figure 2).

This work will be dedicated to the production of jewelry items from zirconia using traditional carving techniques or computerized systems (CNC). First, a full characterization of the material in terms of phases, mechanical properties, toughening, ageing and coloring is conducted.

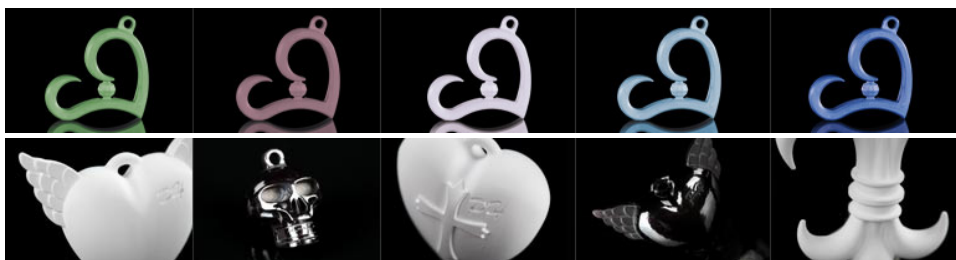


Figure 1 - Machined with the CAD/CAM 5-TEC system from Zirkonzahn.



Figure 2 – Zirconia blank colored zirconia for the production of jewelry (e.g. rings, pendants) and other creative works. The final color is observable only after sintering. <http://www.zirkonzahn.com/pt/produtos/materiais-fresaveis/zirconia-creative>.

2. PHASES OF ZIRCONIA

Zirconia is a polymorphic ceramic with different crystal structure at different temperatures, but keeping the same chemistry. Zirconia can be found in three crystalline forms: monoclinic; tetragonal and cubic, as presented in Figure 3. From this phase diagram we can see that pure zirconia is stable in monoclinic phase at room temperature. At 1173°C it undergoes a phase transformation from monoclinic to tetragonal and then to cubic at 2370°C. Above 2690°C zirconia melts [1].

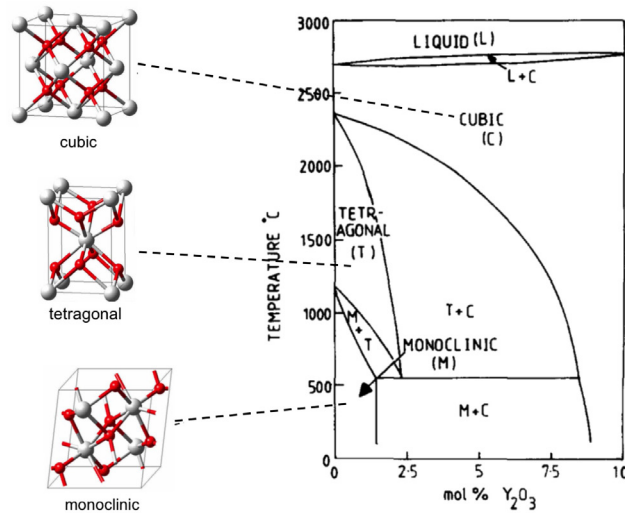


Figure 3 – Phase diagram of the zirconia yttria system.

These transformations are reversible upon cooling with the tetragonal to monoclinic (t-m) transformation imparting compressive stresses to the material due to the volume expansion of 4-5% that occurs with the transformation. As said before, the stabilization of the tetragonal phase is performed when good mechanical properties are required.

Zirconia is most commonly seen in jewelry in the form of cubic zirconia, which is the crystalline form of zirconium dioxide (ZrO₂). This form of zirconia has a close visual likeness to diamond, and therefore it has been an important competitor for diamonds based mainly on its low cost and durability (Figure 4). However, it is not that zirconia that this paper will deal. It will rather deal with the yttrium oxide-tetragonal zirconia polycrystals (Y-TZP), which has a broad field of applications going from restorative dentistry, prosthetics to refractory in gas turbines and thermal barrier coatings in jet engines, among others. The jewelry field has recently arisen as a new field of application.



Figure 4 – Similarity between cubic zirconia (on the left) and a real diamond (on the right)

Source: <http://www.cubic-zirconia-jewelry.com/cubic-zirconia-jewelry>

3. STABILIZATION

It is possible to fully or partially stabilize zirconia in its tetragonal or cubic form at room temperature by alloying it with other cubic oxides termed as “stabilizers” (Figure 5). Calcia, magnesia, Ceria, alumina or yttria are used for that end [2].

Zirconia is said to be partially stabilized (Partially Stabilized Zirconia – PSZ) when a multiphase form coexists in the material: cubic as the major phase and monoclinic and tetragonal zirconia precipitates, as the minor phase.

To date, the best properties are exhibited by zirconia stabilized with Y₂O₃ (yttria), where the whole materials is constituted by transformable t-zirconia grains and called Tetragonal zirconia polycrystals (TZP). The addition of 2-3 mol% yttrium oxide (Y₂O₃) as stabilizing agent results in a fully tetragonal fine-grained zirconia ceramic material with 100% small metastable tetragonal grains (Y-TZP).

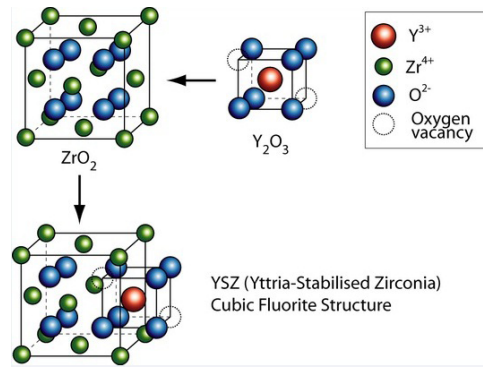


Figure 5 – Stabilization of the cubic polymorph of zirconia (ZrO_2). Substitution of some of the Zr^{4+} ions in the crystal lattice with ions of Y^{3+} . (Source: http://en.wikipedia.org/wiki/Yttria-stabilized_zirconia#cite_note-matweb-2)

4. TOUGHENING MECHANISM

Partially stabilized zirconia displays a toughening mechanism that uses the t-m transformation to arrest the crack propagation, and is therefore termed transformation toughening. When a crack arises in zirconia, the stress field generated in the crack tip cause a local phase transformation from the metastable tetragonal phase to monoclinic phase. This transformation is accompanied to a volume increase of the crystals, constrained by surrounding ones, and a compressive stress field is generated at the crack surfaces near the crack tip that tend to pinch the crack shut, thereby hindering its propagation. The mechanism is demonstrated schematically in Figure 6.

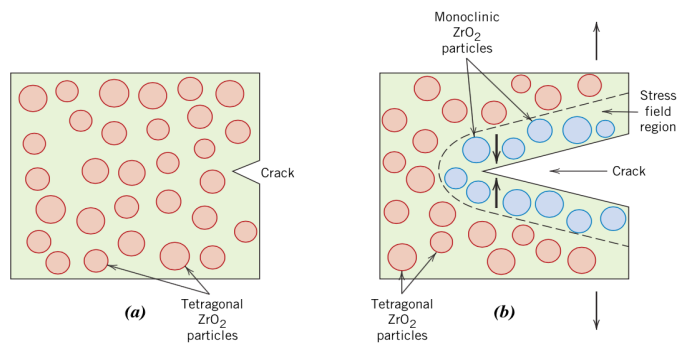


Figure 6 - Schematic demonstration of transformation toughening of zirconia. (a) A crack prior to triggering the ZrO_2 phase transformation mechanism. (b) Crack arrestment due to compressive stresses induced by the t-m phase transformation of zirconia. Source: (Callister, 2014) [3]

5. MECHANICAL PROPERTIES

The mechanical properties of zirconia as compared to other high strength ceramics and stainless steel are presented in Table 1. It is possible to see that mechanical properties of zirconia are higher than those of other high strength ceramic and similar to those of stainless steel. Due to its transformation toughening mechanism, it has a fracture toughness that is almost twice as high as that of aluminum oxide and silicon carbide.

	Flexural Strength (MPa)	Modulus of Elasticity (GPa)	Vickers Hardness (GPa)	Density (g/cm ³)	Poisson's ratio	Fracture Toughness (MPam ^{1/2})
Zirconia, 3 mol% Y2O3, sintered	800 -1500	205	11.7 9 mol% Y2O3	6.0	0.31	7.0 - 12.0
Diamond (natural)	1050	700-1200	130	3.51	0.10-0.3	3.4
Aluminum oxide	282 - 551	380	26.6	3.98	0.22	4.2 - 5.9
Silicon carbide	230–825	207-483	25.4	3.3	0.17	4.8-6.1
Stainless alloy 17-7PH	1310	204	—	7.7	0.3	76

6. COLORING

Zirconia is typically white in color. However, there are methods that are used to pigment zirconia and give it different colors [4-6]. One is the infiltration technique that stains the zirconia frameworks with various metal oxides. Among these oxides we can find the CeO₂, FeO₂, ErO₃, BiO₂. Another method used for this end is the mixing powder techniques, which consists in mixing the metal oxides with zirconia starting powders. Afterwards the material is densely sintered. Both methods are said to achieve similar results, although with slight differences. The infiltration method produces some pigment concentration in the outer surface when compared to the bulk while the mixing technique produces a more homogeneous and stable color.

The black zirconia can be obtained, according to the patent EP 0826645 A2 [7], by the dispersion of at least one of the following group of oxides to the partially stabilized zirconia: MgO, TiO₂, HfO₂, Cr₂O₃, FeO, Co₃O₄, NiO, CO₂NiO₄, NiCrO₃, HfNiO₃, MgCr₂O₄, or CoCr₂O₄.

7. AGEING

Zirconia undergoes a spontaneous process of slow transformation of the metastable tetragonal phase to the more stable monoclinic phase that occurs over time at low temperatures. This process is exacerbated in the presence of water, steam or fluids and is called ageing. It results in a general deterioration of the materials properties, starting from the surface with cracks arising followed by a general loss of strength over the volume of the material in the medium and long term periods [8]. The transformation occurs through nucleation and growth processes. The stage of growth depends on various microstructure patterns, such as: porosity, residual stresses, and particle size, among others. [9]. As jewelry parts are not typically subjected to environments that promotes this phenomenon, this degradation is not expected to occur at level that can compromise the integrity of the piece.

8. MANUFACTURING ROUTE OF ZIRCONIA JEWELRY PARTS

From powders to final pieces some stages are necessary. Figure 7 shows schematically the stages necessary to produce a zirconia piece, namely powder compaction, machining, sintering, and finishing. These stages will be briefly addressed in this paper.

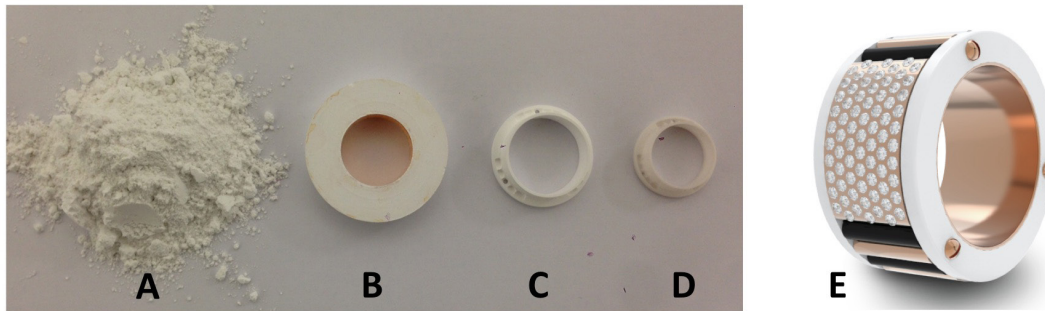


Figure 7 – Several stages of the production of a zirconia component: A) zirconia powder; B) zirconia blank of compacted powder; C) Machined component in green-state; D) Sintered zirconia component; E) Zirconia component assembled in the final jewelry piece of zirconia, yellow gold and diamonds.

8.1 POWDERS COMPACTION

Uniaxial hydraulic pressing is the most common shaping technology for ceramic products [10]. However, when production technologies for new advanced ceramic products with high quality requirements are discussed, in most cases this technology is considered to be only second choice. Other technologies like isostatic pressing seem to provide better quality products, even if it is more expensive, have much lower production capacities or is limited in other factors.

This section describes procedures for shaping of advanced ceramic products using uniaxial hydraulic presses. Some application examples are given.

The main advantages of uniaxial hydraulic pressing technology are the possibility of “dry” pressing along with moderate investment costs. On the other hand, the limitation factors reported for uniaxial hydraulic pressing of advanced ceramics are: only simple geometries are possible; limited dimensions of the specimens to be pressed; comparably high variations in the green density; especially from top to bottom (3...10 % variation are reported); limited dimensional accuracy, e.g. thickness variations in the range of ± 10 %.

Usually, for high quality technical ceramic products, very often uniaxial hydraulic pressing is not at all discussed as a real alternative for shaping in competition to isostatic pressing (cold and hot) [10]. However, it is possible to use hydraulic pressing technology, overcoming the above mentioned limitations. Subsequently, some important aspects of the technology are mentioned, and some characteristic data of samples obtained using this technology are given. In order to achieve an optimum product quality, the following procedures are recommended:

- Feeding of powders to mould; (mould should have air escaping lines for de-aeration);
- Distribution of powders in an almost uniform way;
- Pressing the powders with a slowly pressure increase curve (about 100 MPa per minute) till a maximum of about 200 to 300 MPa, (when vacuum is not used, de-aeration strokes should be used);
- Pressure holding time (2 minutes);
- Pressure decrease curve;
- Ejection.

Among the previous parameters one should be highlighted, namely the use of vacuum. Vacuum plays an important role. Pressing of powders or granulated material in dry, semi-wet or wet condition often results in microstructure inhomogeneities, uneven density distribution and/or formation of layers, even when de-aeration strokes are applied. These effects are mainly caused by entrapped air, due to insufficient release of the air before and during compaction. A well proven solution for this problem is the vacuum pressing technology, where the air inside the material is removed to a certain (selectable) level before the compaction starts. Resulting advantages of vacuum pressing technology are the avoidance of lamination, a higher green density and an even density distribution of the product (Figure 8).

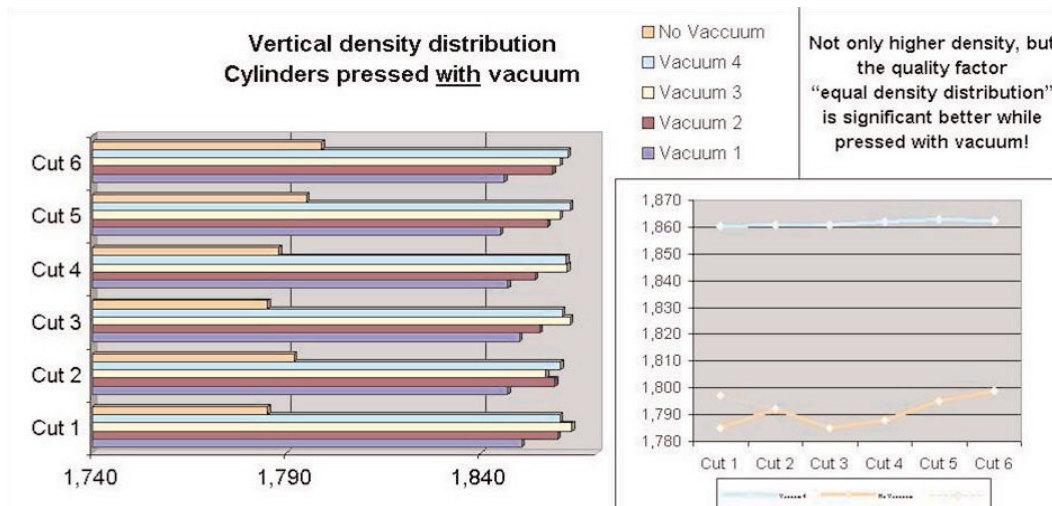


Figure 8 – Comparison of the density distribution of zirconia parts pressed with and without vacuum [10].

Several materials and product dimensions can be obtained only with vacuum technology, whereas conventional pressing technology, even with multiple de-aeration strokes, leads to the destruction of the pressed body after release of the pressure (Figure 9).



Figure 9 - Al₂O₃ sample pressed without (left) and with (right) vacuum (Kaiser, 2007) [10]

Vacuum pressing technology is especially recommended for: granulates with a high densification factor (i.e. mixtures having a low bulk density before pressing and/or reaching a high green density (low residual porosity) after pressing); extremely fine granulates, e.g. very fine spray dried material for technical ceramics; not granulated highly dispersed powders which for conventional pressing technology would have to be granulated; product geometries with large volume or with high aspect ratios (thin plates, rods etc.), where the air needs to move a long distance to the gap between die and mold frame; mixtures with higher plasticity, which are pressed with higher content of water or other liquid binders.

Once a green compact is achieved, the next step is pre sintering or direct machining. Direct machining is undesirable because the green compact, although having some mechanical resistance, may not have enough resistance and cracks may appear, eventually only during final sintering, and sharp edges may also break during machining. The green compact could also be directly sintered and then one could machine it (hard machining). However for use of jewelers it is advised that soft machining is used, after a pre-sintering stage. When properly handled, even with manual presses, reproducibility of the green density has small standard deviations of typically < 1 to 2 % [11]. The surface is very smooth already in the green state. After firing a similar surface quality is obtained with surface roughness typically less than Ra of < 1 µm.

8.2. PRE-SINTERING

Pressed samples are then pre-sintered in, for example, an electric furnace, in air, a stages of 900 to 1100°C for 1 to 2h. Sometimes a debinding stage, at about 500°C, for about 3 h, is recommended. Cycles may change from material to material but, usually, heating and cooling ramp rates of about 60 to 100°C/hour are desirable. Shrinkage of blocks from 0,5 to 2% is enough to give rise to good mechanical properties for a good machining.

Examples of importance of some variables in one granulated Y-TZP powders, containing 5.2 wt% Y₂O₃, 0.25 wt% Al₂O₃, and 3 wt% binder, and crystallite size of 37 nm (TZ-3YSB-E, Tosoh), is presented in Figure 10 [12].

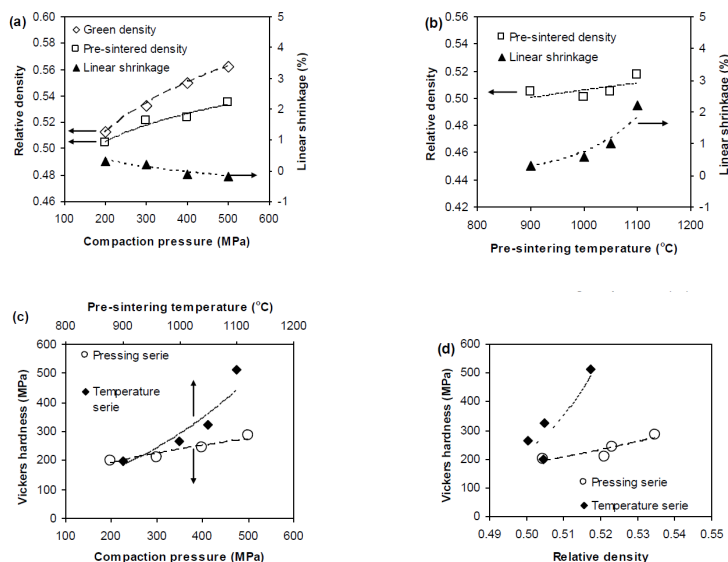


Figure 10 - Results of relative density, linear shrinkage, and Vickers hardness of pre-sintered samples prepared with powder (TZ-3YSB-E). In (a,c,d), pressing series, the pre-sintering temperature was 900°C; in (b,c,d), temperature series, the compaction pressure was 200 MPa. [12]

As expected, the values of relative density and hardness increased with the increase of compaction pressure and pre-sintering temperature (Figure 10). The same trend was observed for biaxial flexural strength [12]. Linear shrinkage was not sensitive to compaction pressure (Figure 10a), but increased with the increase of pre-sintering temperature (Figure 10b). Two distinct correlations were observed for hardness as a function of relative density of pre-sintered samples, depending on the parameter considered, compaction pressure or pre-sintering temperature (Figure 10d). Therefore, pre-sintered blocks with a fixed pre-sintered density and different mechanical properties can be prepared, adjusting the compaction pressure and pre-sintering temperature. Once the blocks are pre-sintered they may be machined.

8.3. MACHINING

Pre-sintered blanks are porous structures. Their machining is easy and can be performed manually with common jeweler tools or using CNC equipment. Soft-machining of partially sintered zirconia ceramic blocs by CAD/CAM technology, to produce dental restorations was proposed in 2001 [13] and since then is being used for different applications including jewelry. The design must compensate for the volume shrinkage that will later occur during sintering of the zirconia pieces. The shrinkage may change depending on the pre sintering conditions but will be about 25%. The partially sintered blocs are easy to mill, which leads to substantial savings in time and tool wear. Tools duration depend also on the pre-sintering parameters and a compromise must be achieved. Higher pre-sintering temperature or time stages increase mechanical resistance but decrease the duration of tools and promote a more difficult machining.

8.4. FINAL SINTERING AND FINISHING

Final sintering occur in an electrical furnace, in air, at sintering temperatures varying from 1350°C to 1550°C and durations from 2 to 6 hours, depending on the material and colour. As an indication different sintering cycles may be used, according to color: White zirconia: 100 °C/ min up to 1450 °C for 2 hours; Black zirconia: 100 °C/ min up to 1400 °C for 2 hours; White zirconia (with alumina): 100 °C/ min up to 1450 °C for 2 hours. However each material has its specific conditions.

Of interest is the fact that the stability and therefore the mechanical properties of 3Y-TZP strongly depend on its grain size [13]. Above a critical grain size, 3Y-TZP is less stable and more susceptible to spontaneous transformation while smaller grain sizes are associated with a lower transformation rate. Grain size is determined by the sintering conditions and particularly the sintering temperature and duration. As shown in Figure 11, higher temperatures and longer durations lead to larger grain sizes.

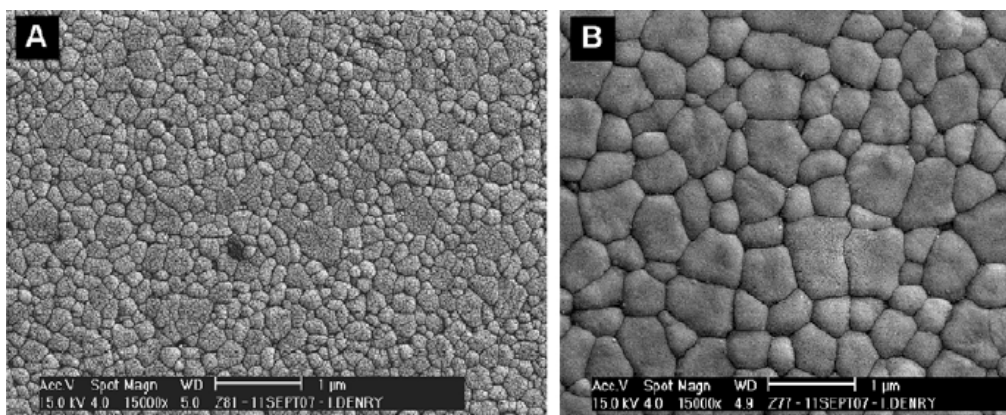


Figure 11 - 3Y-TZP ceramic sintered at (a) 1300 °C for 2 hours and (b) 1500 °C for 2 hours.

Hence, besides the need of a high temperature furnace, no further requirements are needed for sintering of these high tech ceramics.

Although surface finishing of sintered surfaces may be almost polished some finishing operations may be needed, depending of the previous parameters used in the production stages such as machining, powder sizes used, among others. The polishing of the sintered pieces may take place with manual polishing by using clothed discs with diamond suspensions. Other surface finishing may be applied by using sandblasting, laser treatments, etc. Final components such as the ones presented in following figures may be obtained.



Figure 12 - Jewelry pieces with zirconia parts incorporated. Courtesy of Grador®.

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