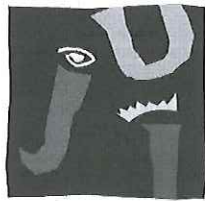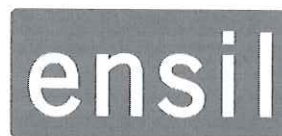Master Final Work - Investigation project (SIT043)

BELKADI Hakima

Bioactive Glass Coatings by Solution Precursor Plasma Spraying

UNIVERSITAT JAUME·I

ensil ÉCOLE NATIONALE SUPÉRIEURE D'INGÉNIEURS DE LIMOGES

Tutor:

Professor Dr. Enrique Sánchez Vilches

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Contents

Introduction

The human body can receive an alien part to replace a broken bone or tooth. Metallic and polymeric prosthesis were first used. Because of the metal oxidation and polymers degradation in the physiological environment of the human body, these prostheses produced additional pain and were rejected by the body. Thus, they were rapidly abandoned. Inert bioceramics, as alumina or zirconia, seemed to be the best alternative thanks to their high chemical stability and their tolerance by the body. However, their high rigidity and the lack of bonds with the human's tissues disqualify them. Further studies lead to more efficient bioceramics with higher bioactivity: bioactive glasses.

The bioactive glasses, which composition is in the oxides system SiO_2–CaO–MgO–Na_2O–K_2O–P_2O_5, were first discovered by L.L. Hench. These glasses can be synthetized by casting and crushing or by sol-gel methods. This kind of ceramics are non-porous and reactive. They can establish chemicals bonds with the bone thanks to its high bioactivity. However, due to the poor mechanical properties of that kind of glasses (are brittle materials), the studies have been developed to obtain a composite of titanium (a metal compatible with the human body's environment) and a bioactive glass coating.

In order to obtain a totally vitrificated coating, various coating techniques can be used, but the most efficient is the thermal spraying with an atmospheric plasma. The bioactive glass made via sol-gel or casting and crushing methods can be sprayed as powder or in a suspension, but also as a liquid solution before the gelation point, developed by the sol-gel.

In this study, the SiO_2–CaO–Na_2O–P_2O_5 bioactive glass is synthetized as a solution by the sol-gel technique and then sprayed by an atmospheric plasma onto a steel substrate, in order to develop preliminary coatings. Spraying the solution gives better results than spraying the powder or the suspension, regarding the coating particles' size. It is very important to master the parameters of the synthesis, because any changing in the composition can alter the bioactivity of the bioactive glass. This is why the composition of the bioactive glass obtained need to be determined. Moreover, the spraying's optimal parameters need to be calibrated to produce the ideal coating. Finally, characterisation techniques, such as thermogravimetric analysis and X-rays diffraction, are used to analyse the solution, and the Scanning Electron Microscope to analyse the coating. These techniques will show the amorphous character of the bioactive glass and the microstructure of the coating obtained.

I. Bibliographic Review

A. Biomaterials

1. History

To replace human bones or teeth, many materials can be used, such as metallic, polymeric and ceramic materials. A lot of progress has been done in this field to obtain the best materials to replace diseased or damaged tissues, which must be accepted by the body and in the meantime, they should possess good mechanical properties. Among all the types of biomaterials, ceramics have shown the best tolerance by the body, since it is possible to employ ceramics with a composition similar to that of bones. Moreover, these materials must be harmless to humans, indeed they cannot have any toxic or cancerogenic element in their composition. [1]

The biomaterials can be classified into three separate groups [2], with different properties according to their final application. The first group is formed by the bio-inert materials. This means that the material does not react in any form with the body. It does not change with the time and the body tissues develop around it. An example of such type will be zirconia or alumina for teeth prostheses.

The second group is composed by the bioactive materials. They link with the body tissues, which give them better mechanical properties than the bio-inert ones. Their surface will react with the biological fluid which allows the bone to reform. Since they contain the same elements than the bones, the elements in the surface dissolve and help to form the bone just above the surface.

The third group is composed by the resorbable biomaterials. This means that they will react with body tissues forming bonds, just like the bioactive materials. But with time their contact with the body fluids will make them totally dissolved, disappearing while the bone will reconstruct it-self instead of it. This type of biomaterial seems to be the best one, but it is more complicated to use because the biomaterial disappearing velocity needs to be the same velocity than the bone forming velocity, to allow the replacement. Moreover, it cannot always be used because some body parts need to have always good mechanical properties. For example, the skull prostheses must be bio-inert or bioactive only, in order to protect the brain from the exterior pressure.

From all categories described above, nowadays the most studied group is the bioactive one, and especially from this group the bioactive glasses.

2. Bioactive glasses

2.1 Description

The first bioactive glass was developed by L.L Hench in a project with the US Army Medical Research and Development [8]. He started studying SiO_2-CaO-Na_2O diagrams to which he added 6 wt % of P_2O_5. Hence, he discovers the first bioactive glass named 45S5 or Bioglass®. Its composition is 45% SiO_2, 24.5% CaO, 24.5% Na_2O and 6% P_2O_5 (in weight percentages) and the molar ratio of Ca/P is equal to 5.

The bioactive glass 45S5 is typically produced by the melting and quenching method. This is why Na_2O is introduced into the glass composition, in order to decrease the fusion temperature of the composition. After the fusion process, the obtained melted is cooled rapidly in water to prevent crystallization. [2, 3]

In order to avoid high temperature processes and the impurities that can be added to the glass during the different steps of manufacturing (quenching, crunching…), the sol-gel method started to be investigated with the aim of produce this type of glasses [4]. The high purity of the raw materials and the manufacturing technique are very important in the final bioactivity, since the high specific surface area of the final product increase dramatically the capacity of reaction with the biological environment. In the next section, this method is described.

The bioactive glass 45S5 peculiarity, is to develop a layer of carbonated hydroxyapatite (HAC) very similar to the bones composition, when they are in contact with the body fluids and tissues [4]. This layer allows the increase of the adherence between the prosthesis and the body's cells. The bioactive glass 45S5 was tried first in vitro in a Simulated Body Fluid (SBF) and then in vivo in a rat's femur and tibia and in monkey limbs [1, 3].

The SBF is used to evaluate the in vitro bioactivity of the samples as mentioned in the last paragraph, because it has an ionic composition similar to that of the human blood plasma [5-8]. It is widely used for testing the dissolution rate of bioactive materials. There is a reaction of SBF with bioactive glass: HCA forms on the surface of the glass which is necessary for osteo-production. In the literature, this test is usually practiced on the synthetized bioactive glass, which is immersed into the SBF at 36.5°C (the body temperature). At the end of the experiment, the powder is rinsed with deionised water to avoid more reaction and dried at 70°C. Then the amount of crystallized HCA is measured to define the bioactivity index of the synthetized bioactive glass.

L.L Hench defined the bioactivity index I_B to assess the bioactivity of a given material. [5] This index is calculated by equation 1, considering the variable $t_{0.5}$ as the number of days needed for the bioactive glass to bond with 50% of the bone.

$$I_B = 100/t_{0.5}$$
(Eq. 1)

Hench work has demonstrated that a glass need to have at least 60 wt% of silicon as a forming element, an important amount of Na_2O and CaO as modifiers and an elevated molar ratio of Ca/P in order to show bioactivity [8].

Based on the above, the SiO_2-CaO-Na_2O diagram with 6 wt% of P_2O_5 (figure 1) [4], can be divided into four zones in function of the glass composition. The A-zone contains the compositions that leads to bioactive glass. This zone is separated in various subzones delimited with iso-index of bioactivity with indexes from 0 to 10. The other zones don't lead to bioactive glass, because the B-zone gives glass with too much surface reactivity, the C-zone glass surface has too poor reactivity and the D-zone compositions cannot lead to glass.

The bioactive glass indicated in the centre of the A-zone is the 45S5 developed by Hench.
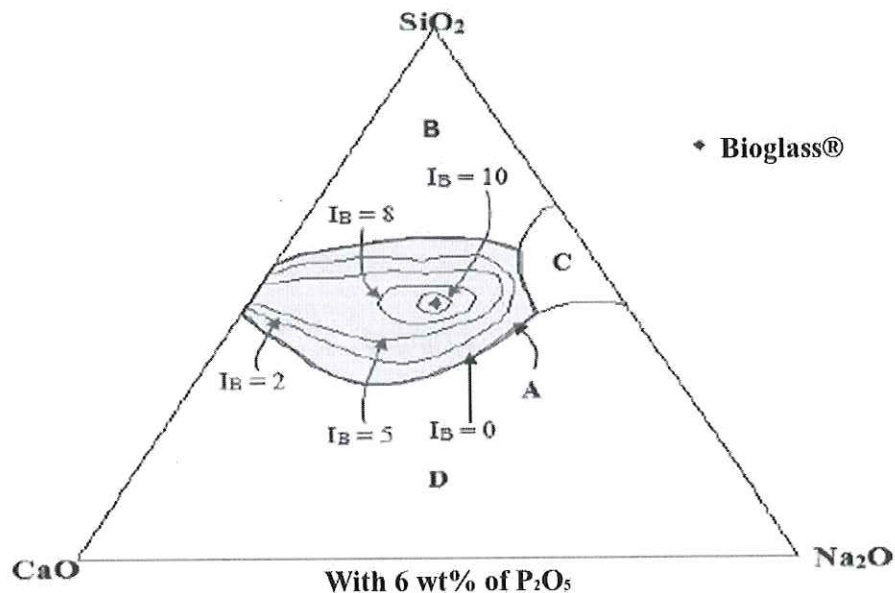
Figure 1: SiO2-Na2O-CaO diagram with bioactivity index

2.2 Applications

The first prosthesis of Bioglass® in the human body was a middle-ear prosthesis [2] fabricated in 1985. Then, it was used in head and neck surgery. This bioactive glass was man-ufactured by casting and crushing and for their use, they did not need to have very high me-chanical properties. Indeed, the limited mechanical strength and low toughness of bioactive glasses has prevented their use as load bearing devices. Research were then conducted to develop a bioactive glass composites that have the same bone bonding characteristics of 45S5 bioactive glass.

Nowadays, bioactive glasses can be used in many applications as mentioned above. Some examples are described below [1]:

- Solid shapes (bulk material, composite)

The glasses can be fabricated by casting into shaped implants for specific purposes where mechanical strength is not important, for example a middle-ear device (fig 2-A) [1] or to fill the defect in the jaw bone when a tooth is removed, with cylindrical bioactive glass (fig 2-B) [1].
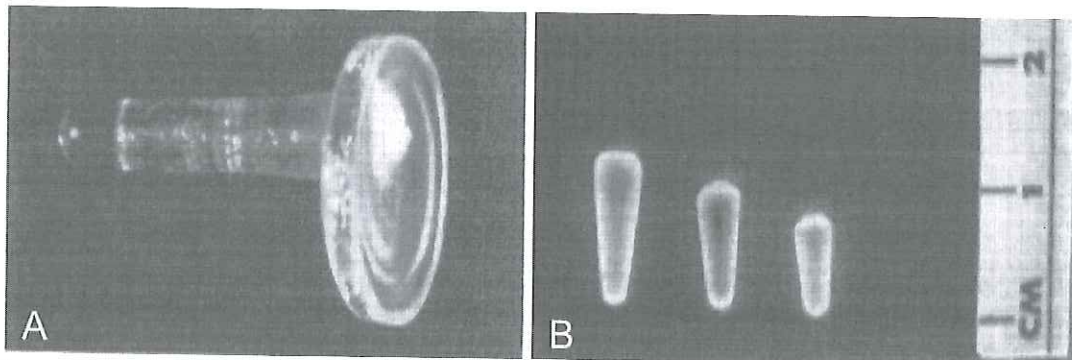

Figure 2: Examples of solid bioactive glass application, (A) Middle ear device, (B) Jaw bone filler

- Particulates of various size ranges

Bioactive glass in the form of particulate has found application in the treatment of periodontal disease. An infection that attacks the mouth gum can reach the bone and destroy it and leading to the loss of the teeth. To avoid this, surgery combined with antibiotics are used, but the bone needs also to be repaired and connected to the soft tissues. Investigations were led to use this bioactive glass to treat vocal cords paralysis. [1]

- Particulates combined with the patient bone particles

The success of particulate material in restoring bone in the periodontal area lead to a series of investigations in which the glass has been mixed with autologous bone before implanting. The best material for restoring lost or damaged bone for reconstructive and cosmetic reasons is undoubtedly fresh bone from the patient, which carries none of the potential problems of rejection or viral contamination. A mixture of bioactive glass granules and autologous bone chips has also been used in situations where the amount of bone is insufficient for dental implants to be inserted (figure 3) [1].
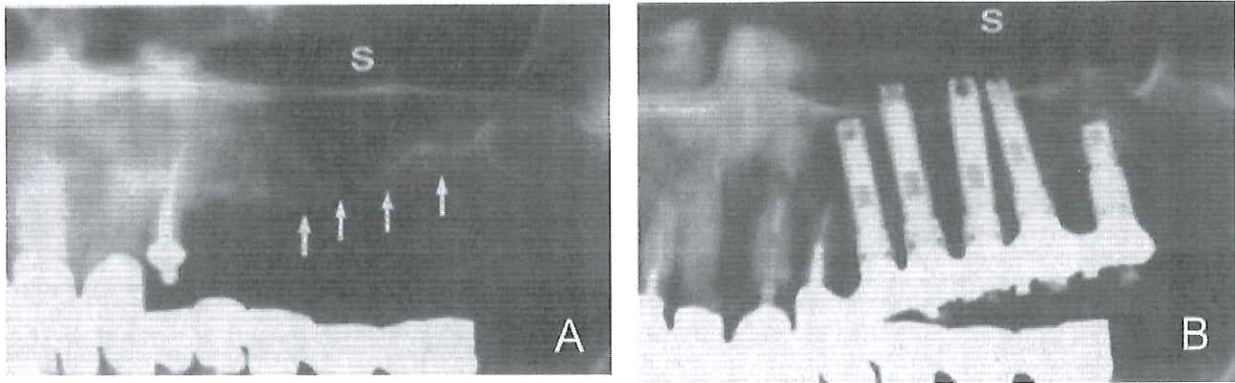
Figure 3: Radiograph of a 69-year old woman shows that the amount of bone in the area of left maxillary sinus (S) – (A) insufficient to support dental implants (arrows)- (B) six months after insertion of implants of S53P4 bioactive glass shows considerable increase in the amount of bone on the floor of the maxillary sinus

- Particulates delivered via an injectable system

Another group of applications are those which depend on the soft tissue adhesion of these materials and which are facilitated by the ability to introduce them by injection. But there are various complex parameters (particles size and shape, the needle size, the vehicle characteristics) that need to be mastered to avoid further problems. Now a day only clinical tests on animals are run to treat urological conditions. Clinical trials need to wait until the development of a satisfactory combination of materials and delivery system. [1]

In the table 1 [1], there are some commercially used bioactive glass with their composition and the manufacturing techniques. Thus, casting and crushing technique was first used to obtain this bioactive glass, but the sol-gel method starts to appear more interesting to this purpose because of its soft work conditions comparing with casting and crushing.

Table 1: Common Bioactive glasses' composition and manufacturing technique

Commercial Name	Composition (% Molar)	Process of fabrication
45S5 (Bioglass®)	46.1%SiO_2 – 24.2% Na_2O – 26.9% CaO – 2.6% P_2O_5	Casting and crushing
S53P4 (BonAlive®)	53.8%SiO_2 – 22.7% Na_2O – 21.8% CaO – 1.7% P_2O_5	Casting and crushing
13-93	54.6%SiO_2 -6.0% Na_2O – 22.1% CaO – 1.7% P_2O_5 – 7.9%K_2O – 7.7%MgO	Casting and crushing
58S	60%SiO_2 –36% CaO – 4% P_2O_5	Sol-gel
S7030C	70%SiO_2 – 30% CaO	Sol-gel
MBG85	85%SiO_2 – 10% CaO – 5% P_2O_5	Sol-gel
B75-Sr5	75.5%SiO_2 –21.6% CaO – 2.9% SrO	Sol-gel

3. Bioactivity of the bioactive glass

The bioactive glass is a bioactive material which forms bonds with the body tissues and whose surface reacts with the body biological fluids to help the bone grow. In fact, the silicon present in the glass, will form a gel near the surface and will act as a nucleation catalyst to a carbonated apatite [4].

As seen in figure 4 [4], the bioactivity is conducted by the partially dissolution of the bioactive glass surface and the development of HAC layer similar to the bone's mineral. This dissolution changes the chemical composition, the PH, and the thermodynamic equilibrium.

All that induces the nucleation of calcium phosphate on the glass surface. The dissolution's kinetic must be controlled and synchronised with the cellular changes of the wound tissues. If the chemical release rate is too fast, the concentration of ions will be too high to be effective. If it is too slow, the concentration will be too low to stimulate cellular proliferation [1].

The physico-chemical mechanism described in figure 4 [4] is divided into five steps:

First step:
- Alkaline and alkaline-earth ions (Na, Ca^{2+} ...) and phosphate ions pass from the glass's surface to the physiological liquid
   - Hydrogen ions arrive from the body fluid to the glass surface
   - Silanol groups Si-OH forms and the zone's PH increases

Second and third Steps:
- The PH increase hydrolyses the Si-O-Si bonds
- Soluble Si-O groups are liberated in the fluid and Si-OH groups forming on the surface
- A SiO_2 gel is forming on the top of the glass

Fourth step:
- The lack of alkaline and alkaline earth makes the Ca^{2+} ions to migrate through the SiO_2 layer
- An amorphous calcium phosphate layer grows

Fifth step:
- The calcium phosphate layer incorporates OH and carbonate groups and partially crystallized into a carbonate hydroxyapatite, similar to the bone
- The new layer tends to transform into the thermodynamically more stable apatite, commonly called "biological apatite"
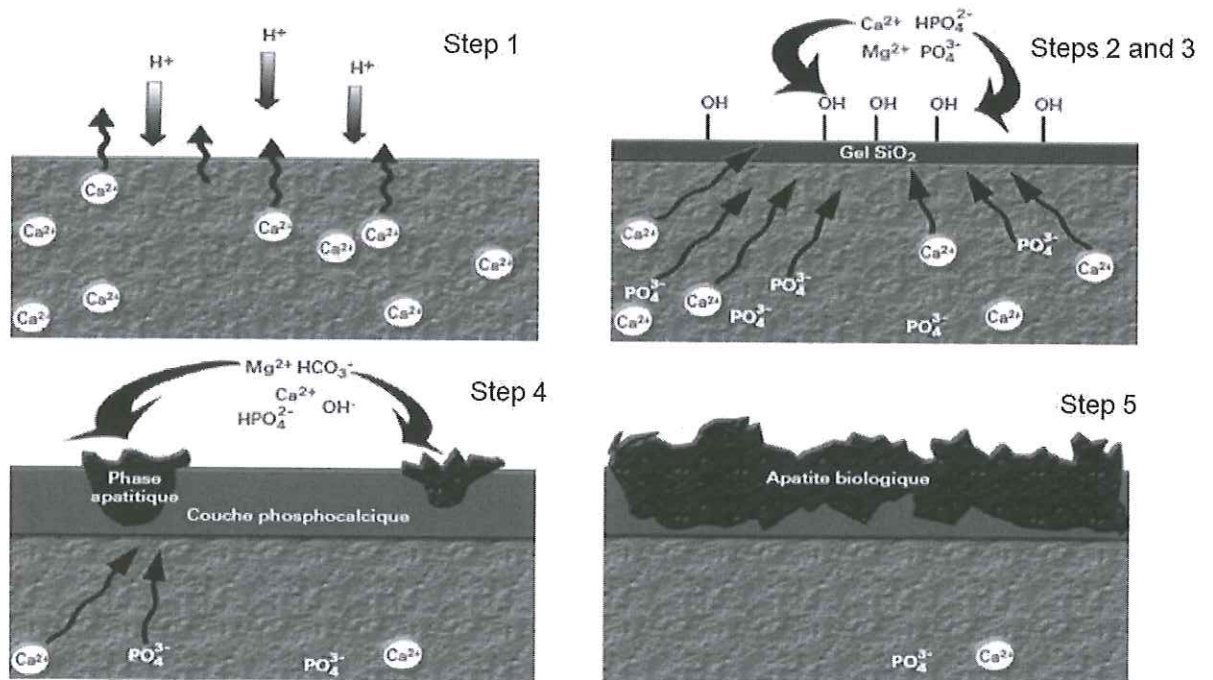
Figure 4: Apatite formation mechanism on the bioactive glass surface

This mechanism has been followed through SEM images (figure 5) [4]. The first image (figure 5-a) is taken from the initial state of the glass, which shows a very smooth surface. Then the bioactive glass has spent one day in contact with SBF. After that time, precipitates appear and the surface has lost it smooth aspect (figure 5-b). Finally, in the last picture (figure 5-c) it can be appreciated the surface of the reacted glass after 1 day in SBF at more magnification, showing the porous calcium phosphate structure on the bioactive glass surface. [4]

(a) Initial bioglass surface aspect (Mag X10 000)

(b) bioglass surface aspect after 1 days immersion in the physiological fluid (Mag X10 000)

(c) bioglass surface aspect after 1 days immersion in the physiological fluid (Mag X30 000)

Figure 5: SEM micrographs of a bioactive glass' surface initially and after one-day immersion in a biological fluid

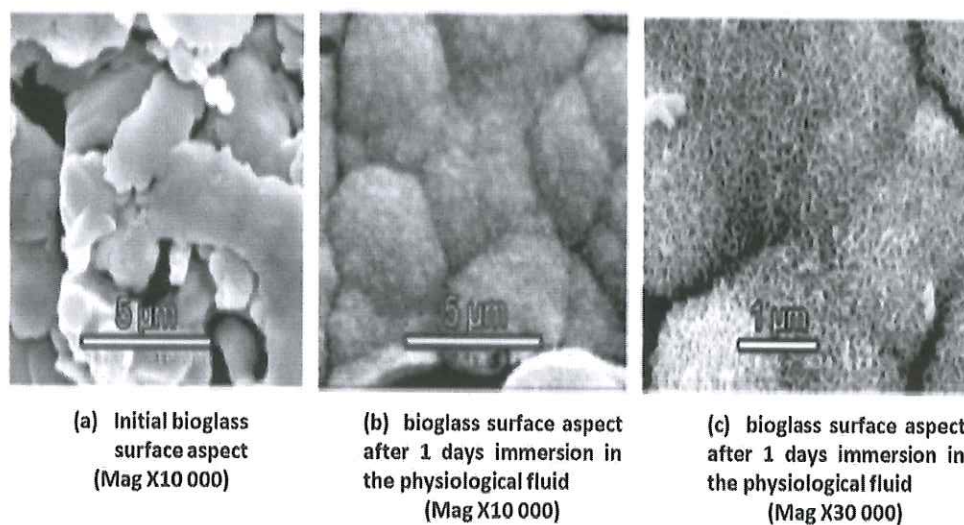Biomaterials enable high interfacial reaction rates between the host tissue and the implanted material in the body. Consequently, the bioactive glasses can be classified into two categories [2]:

- **Class A**

The class A bioactive glass surface reactions involve ionic dissolution of critical concentrations of Si, Ca, P and Na ions. That give rise to both intracellular and extracellular responses at the interface of the glass with its physiological environment, which leads to both **osteoconduction** and **osteoproduction.**

- **Class B**

The Class B bioactivity occurs when only **osteoconduction** is present, with only extracellular responses of the bioactive glass surface.

As seen earlier, bioactive glass materials are available in a range of compositions and implant shapes which are able to bond to soft tissues and to bones. These materials can have different reactivity and speed of bonding. They have been successfully applied as solids materials and particulates and may be combined with both natural and synthetic materials, to provide treatment for many clinical conditions.

B. Sol-gel technique

1. Presentation

The sol-gel manufacturing method is considered as a "soft technique", because it does not imply using high temperatures. It is also considered as an economical technique that produce high quality products. Thus, the materials can contain organic or biomolecular components. It has been used in many various fields such as the fabrication of optical materials, electronics, sunscreen creams and in bioactive materials as mentioned in the first section of this work.

At first, the sol-gel method was used in the ceramic sector mainly to produce homogenous powder. However, the sol-gel reactions mechanism was not studied. The first whose investigated these mechanisms was the nuclear sector, that wanted to use this technique to produce small spheres of radioactive oxides without producing dangerous dust. But the studies were not published. The technology was not investigated properly by the ceramic fields until the sixties. Since then a lot of published work has been done, and the technique is now a day a well-known method.

The sol-gel synthesis is based on a succession of hydrolysis and condensation reactions, which allows to form amorphous oxide structures at low temperature, and then stabilized them by thermal treatments [9].

Using the sol-gel technology to make biomedical materials is ideal, because this soft synthesising technique allow to keep the bioactivity of the material. In addition, the high specific surface area of the obtained material increases its reaction rate. Many studies compare the casting and crushing technique to the sol-gel method. Contrary to casting and crushing, sol-gel method allows to have [10]:

- Low fabrication temperature means quality and cheaper product

- More control on the composition

- Higher specific area which increases the dissolution rate in body fluid and the bioactivity

One of the technique drawbacks is the fact that devitrifying is possible, so the product is more likely a glass-ceramic with various crystalline parts, which is considered less bioactive because it is more stable thermodynamically. But scientists [10] show that the higher specific area allows the increase of the rate of hydroxycarbonate apatite (HCA) formation, which is essential for preparing a suitable environment for attachment and differentiation of stem cells. Moreover, if the glass structure is needed exclusively, as in the bioactive glass, it can be obtained using techniques that do not allow the crystallization such as thermal spray coatings.
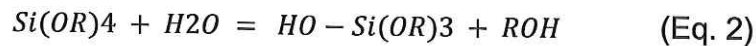
2. Reactions

2.1 The sol

A sol is a colloidal suspension, which means that it is composed of solid particles of a size between 1 and 1000 nm in a liquid continuous phase. With such size, the particles are more sensible to the Van de Waals attraction and surface charges interactions than to the gravitational forces. Because of their size their movement is driven by random collisions with other particles. This movement is called Brownian motion. [11]

The sol can be used in the fabrication of ceramic materials. The precursors used in the sol-gel technique are generally metals or metalloids atoms surrounded by various ligands. The precursors can also be inorganic salts or even organic compounds, such as alkoxides [12].

This last type of precursor is a compound with a mix of an alkyl group ($-C_2H_5$ for example), and a hydroxyl group (-OH) without the proton, forming a group of alkoxy ($-O-C_2H_5$). These precursors are metal alkoxides and they have in general a metal or metalloid atom with a direct bond with an oxygen, which is also linked to a carbon. A well-known and used metal alkoxide in the sol-gel sector is tetraethyl orthosilicate (TEOS), and is used as a precursor for silica.
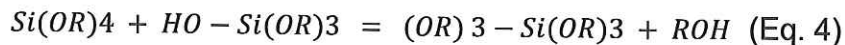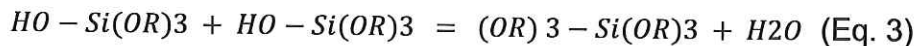
The metal alkoxide are widely used because of their direct reaction with the water: **hydrolysis**. This reaction leads to the formation an -OH group that replace one of the alkoxy groups. Depending on the amount of water and catalyst, the hydrolysis can be more or less advanced and the alkoxy groups may be partially or totally replaced. [12]

For example:

$$Si(OR)4 + H2O = HO - Si(OR)3 + ROH \qquad \text{(Eq. 2)}$$

Two partially hydrolysed metal alkoxides can link together and form a larger molecule liberating a small molecule. This reaction is called **condensation**.

For example:

$$HO - Si(OR)3 + HO - Si(OR)3 = (OR)3 - Si(OR)3 + H2O \text{ (Eq. 3)}$$
$$Si(OR)4 + HO - Si(OR)3 = (OR)3 - Si(OR)3 + ROH \text{ (Eq. 4)}$$

While the condensation is going on, large molecules containing silicon are formed. Moreover, TEOS fully hydrolysed can have condensation with the four -OH groups and it will have a very complex and three-dimensional structure.

2.2 The gel

The gel point is the moment when the last bond that complete the first macromolecule is made and takes place after the condensation step. Other macromolecules are formed and linked to one another forming the solid structure. This structure is also called the spanning cluster. The obtained gel has a solid structure enclosing a continuous liquid. The continuity of the solid gives elasticity to the gel. The condensation does not stop when the gel point is reached, there is still sufficient elasticity to allow the condensation to continue and the little molecules presents in the remaining sol, link with others and with the network [11, 12].

The gelation is the result of the colliding of macromolecules formed by hydrolysis and condensation and the formation of links between those macromolecules. The gel that is formed is described as weak or strong depending on the fact that the bonds connecting the macromolecules is permanent or reversible. The gelation corresponds to the time that the macromolecules in the sol are forming links and connecting one to the others. When the last link between macromolecules is formed, the gel appears.

What is called gel aging is a process that occurs after the gelation by polymerisation, coarsening and phase transformation. There is for example the formation of Si-O-Si bonds from two groups of Si-OH. This occurs with liberation of water. Such reactions create silicon bridges and increase the gel stiffness. But there can also be more hydrolysis or the hydrolysis reverse reaction: the esterification (which corresponds to the liberation of an alcohol and forming the initial Si-OR bond). But this last non-desired reaction is slow down by an excess of water. [12]

The gel can undergo a shrinkage, called syneresis, while the molecules are getting closer and evacuate the liquid enclosed between them. This leads to decrease the pores size. But the shrinkage can also occur during the drying process by capillary pressure. As shown figure 6 [12], the just dried gel is called xerogel. The shrinkage needs to be taken into account, because it involves deformations in the network. To avoid the deformation during the drying, the gel can be dried in autoclave. The dried gel with solvent extraction is called aerogel. Such a gel can be used to make porous ceramics materials or in order to make ceramic powders.
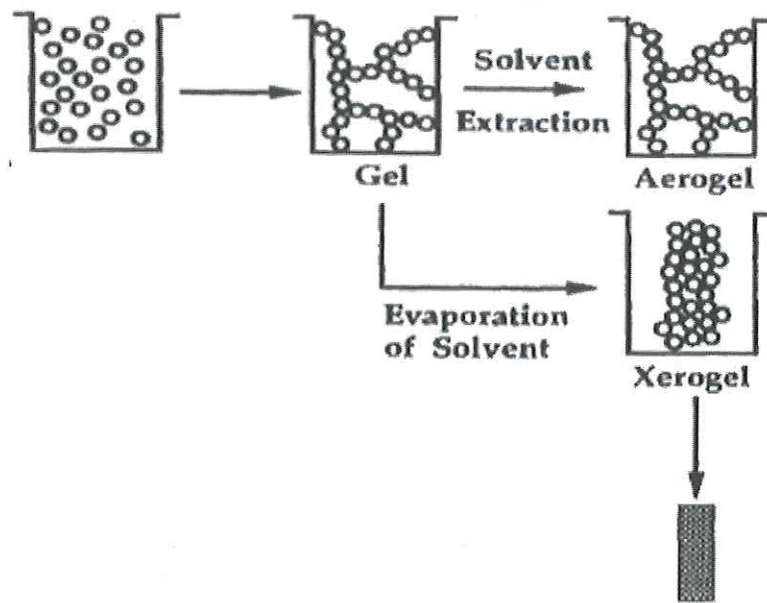
Figure 6: Gel drying with evaporation of solvent or with solvent extraction

Most gels are amorphous after drying but they might crystallize once sintered. If the desired material is amorphous, the sintering technique needs to be chosen to avoid the crystallisation.

Sol-gel method can be used in different forms to obtain various kind of materials (figure 7) [11]:

- After drying and stabilizing, a monolith of the ceramic material can be obtained.

- As a coating of a thin layer on a substrate.

- Gelation on a porous substrate, it will lead to a macro-porous product with a controlled porosity, after the elimination of the substrate.
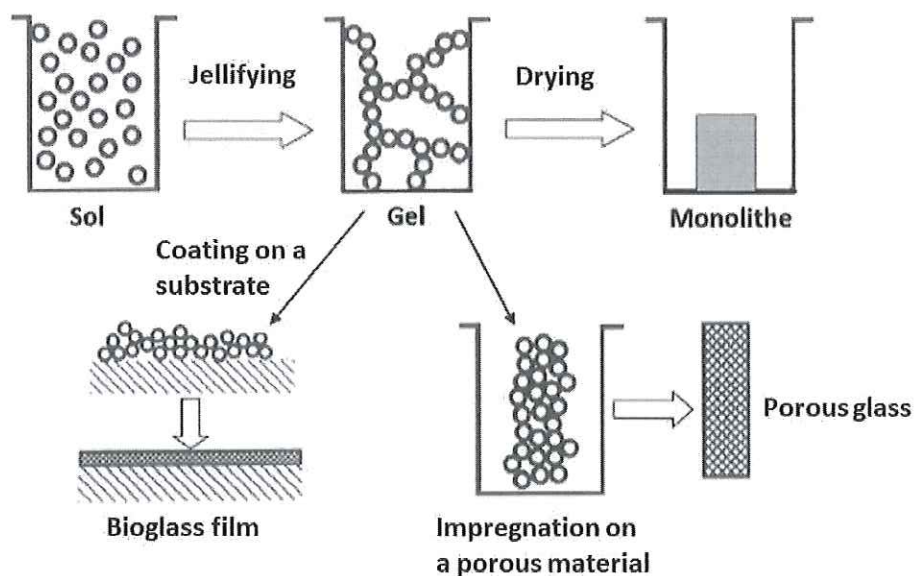
Figure 7: Different ways of obtaining bioactive glass from a sol-gel technique

2.3 Thermal treatment

In order to stabilise the desired material, the gel needs to be heated at a temperature between 500°C and 1000°C. The thermal treatment allows to evaporate all residual solvent and unnecessary organic compounds. If there is micro-porosity, it will become larger. [11]

3. Sol-gel in the bioactive glass fabrication

As mentioned above, the sol-gel method can be used in the fabrication of bioactive glasses. To obtain a bioactive glass with this technique, it is very important to choose the precursors carefully. Consequently, it is essential to understand how every component react. Many studies explain the role of every precursor in the reactions. As seen before, the bioactive glass composition is CaO (24.5 wt%), P_2O_5 (6 wt%) in a Na_2O-SiO_2 matrix (24.5 and 45 wt%) [9].

3.1 Glass structure Forming elements

The silicon is introduced as the alkoxide TEOS or sometimes as TMOS. The selection of one or the other, modifies the kinetic of gelation because of the different substitutions it induces during the hydrolysis-condensation reaction [11]. Indeed, on this parameter the size of the chain has a significative influence. Many studies on bioactive glass obtained by sol-gel

method use TEOS. This precursor has the ability of hydrolysing easily and one or more group can be changed from Si-Et to Si-OH (figure 8) [11].
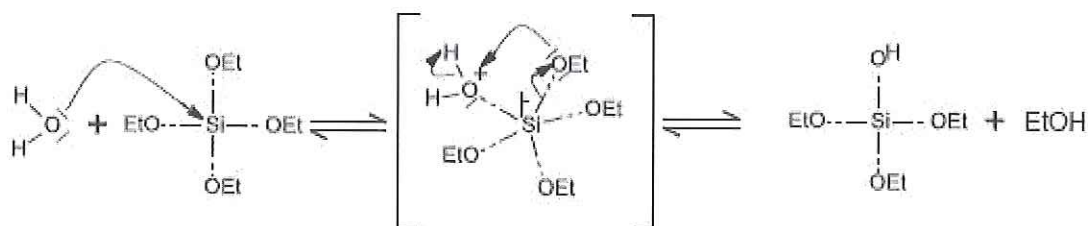

Figure 8: The mechanism of hydrolysis of TEOS with H_2O

As seen in the mechanisms both the hydrolysis and the condensation (explained later) are done with a nucleophile substitution. Indeed, the mechanisms shows first a nucleophile addition followed by a proton transfer. The thermodynamics of this reactions is governed by the strength of the nucleophile (H^+ is stronger than H_2O), the electrophilicity of the metal in table 2 [12], which means that transition metal alkoxide are hydrolysed faster than the TEOS. But it also depends on the charge and stability of the leaving molecule.

Table 2: Positive partial charge δ(M) for metals in various Alkoxides

Alkoxides	$Zr(OEt)_4$	$Ti(OEt)_4$	$Nb(OEt)_5$	$Ta(OEt)_5$	$VO(OEt)_3$	$W(OEt)_6$	$Si(OEt)_4$
δ(M)	+0.65	+0.63	+0.53	+0.49	+0.46	+0.43	+0.32

Moreover, the amount of water regarding the amount of TEOS is also a very important factor. In fact, if the molar ratio water/TEOS is high, the hydrolysis will be faster. This is shown in figure 9 [12], as the ratio increases the time of gelation is decreases rapidly. Therefore, this ration needs to be chosen as a parameter of the solution just like the catalyst amount to obtain a sol-gel with the desired gelling time.
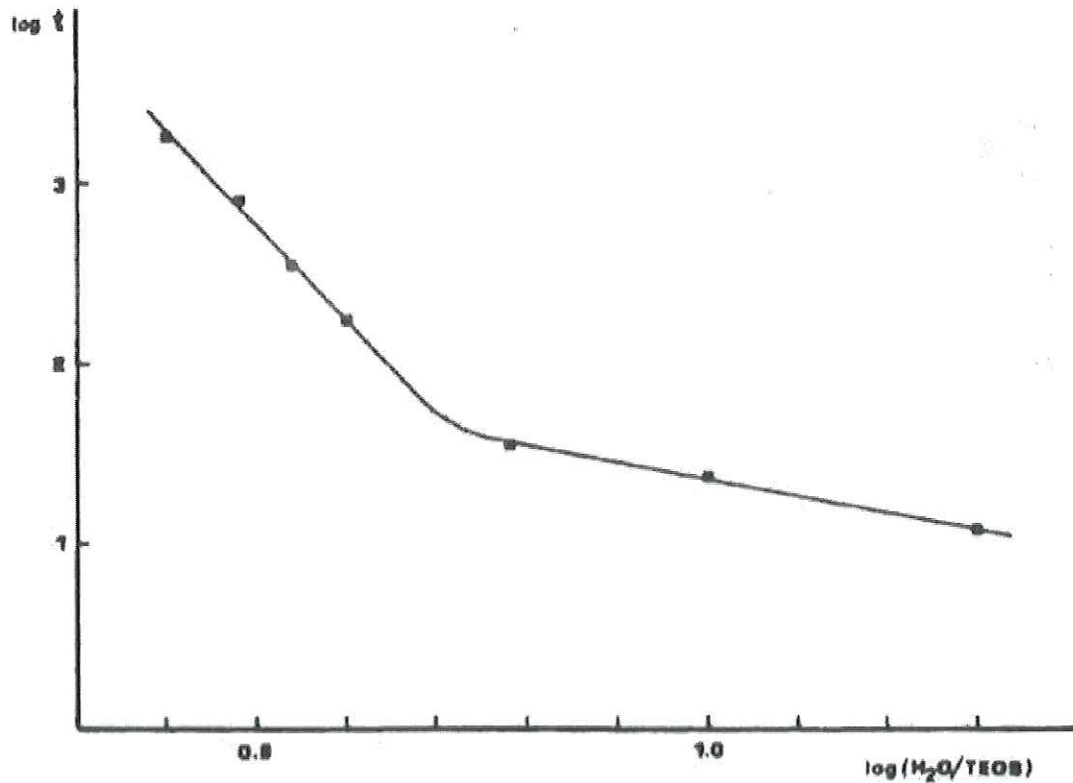
Figure 9: Curve of logarithm of gelling time (hours) versus log([H₂O]/[TEOS])

Then, there is the condensation reaction, which is also a nucleophile substitution and depends on the same factors. The condensation can occur in two different mechanisms:

The **oxolation**, where two groups -OH combine to give a H_2O molecule and a silane bond Si-O-Si (Figure 10) [11].

Figure 10: The Oxolation mechanism

The **alkoxolation**, where a group -OH combines with a group O-R of the alkoxide to give an alcohol and a silane bond (figure 11) [11].

21

Figure 11: The Alcoxolation mechanism

The second important glass structure forming [13] is the phosphorus. It is fundamental to the bioactivity because it is a main component in the human bone with the calcium. To introduce this element in the bioactive glass, the precursor mainly used is th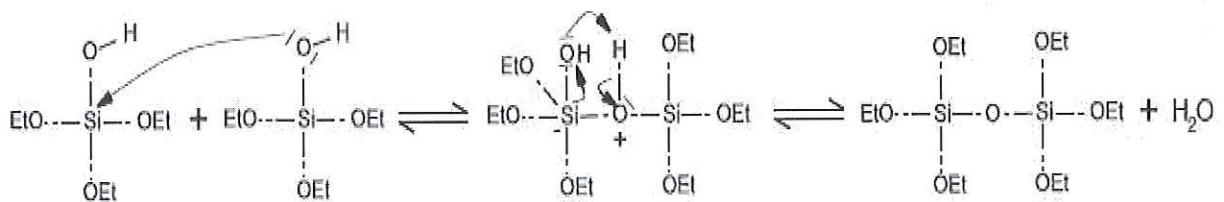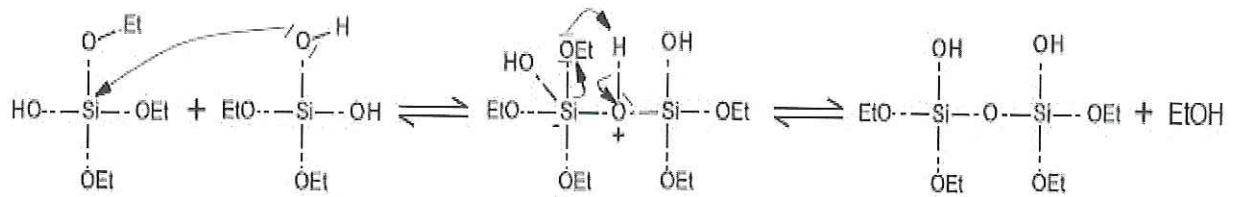e TEP (Tri-Ethyl-Phosphate). But sometimes the phosphoric acid can also be used. The hydrolysis of the TEP is very similar to the hydrolysis of the TEOS (figure 12) [11]. it is also followed by a condensation reaction that will create long chains to be linked with the main chain structure.
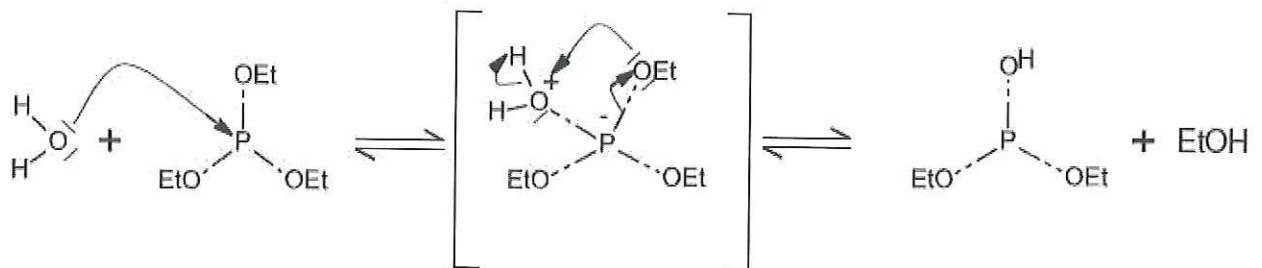

Figure 12: Mechanism of the hydrolysis of the TEP

3.2 The glass structure modifiers

The sodium is also an important element in the bioactive glass, it is present as Na_2O. This oxide is also present in common glass [13] and permit to decrease the glass elaboration temperature to 1400°C. But it can also break the Si-O bond, leaving the structure more fragile and more soluble in aqueous sites. Which may appear as a problem for common glass is an advantage for bioactive glass. Indeed, when the prosthesis is in the body in contact with the physiological liquid, the glass surface is more likely to dissolve and a hydroxyapatite structure will nucleate and grow upon it [13].

The sodium is introduced in the sol as sodium nitrate ($NaNO_3$). It is added at last, it diffuses in the high viscosity solution and when the solvent evaporates, the sodium salt precipitate. Other precursors can also be used as sodium alkoxide that can be hydrolysed just like the other alkoxide in the sol, such as sodium acetate CH_3COONa.

The calcium is considered as glass structure stabilizer [13], it is present in the glass as CaO. Various precursors can be used to add this component to the bioactive glass. For example, it can be introduced as mineral salt such as calcium carbonate and calcium nitrate.

The carbonate and the nitrate precursors have the advantage to be easily eliminated in the thermal treatment.

C. Thermal spray coating

1. Presentation

Coating is an engineering solution to enhance surfaces against wear, corrosion or thermal degradation. Moreover, coating techniques can be used to add properties to the substrate. For example, a coating can bring new mechanical, chemical or biological properties. Coatings allow to do all that without replacing the whole piece, thus it can also be considered as an economical solution. Generally, the desired coatings are characterised by good adhesion, substrate compatibility, and controlled porosity. An acceptable coating process must also be compatible with the substrate shape [14-20].

To choose a coating method it is important to consider the process performance and the coating requirements. There are many coating techniques classified with the energy origin and the sprayed material. They can be chemical or physical processes and lead to different coatings shape and characteristics. In figure 13, some of the most used coating techniques are classified with the intervals of coating thickness they can reach. For example, the physical vapor deposition (PVD) can deposit coatings until 100 μm while thermal spraying techniques will give larger coatings thickness figure 13 [21].

Layer thickness	0,1 μm	1 μm	10 μm	100 μm	1 mm	10 mm

Electrolytic deposition

Electropolymerizing

PVD, CVD

Thermal Projection

Galvanisation

Laser Cladding
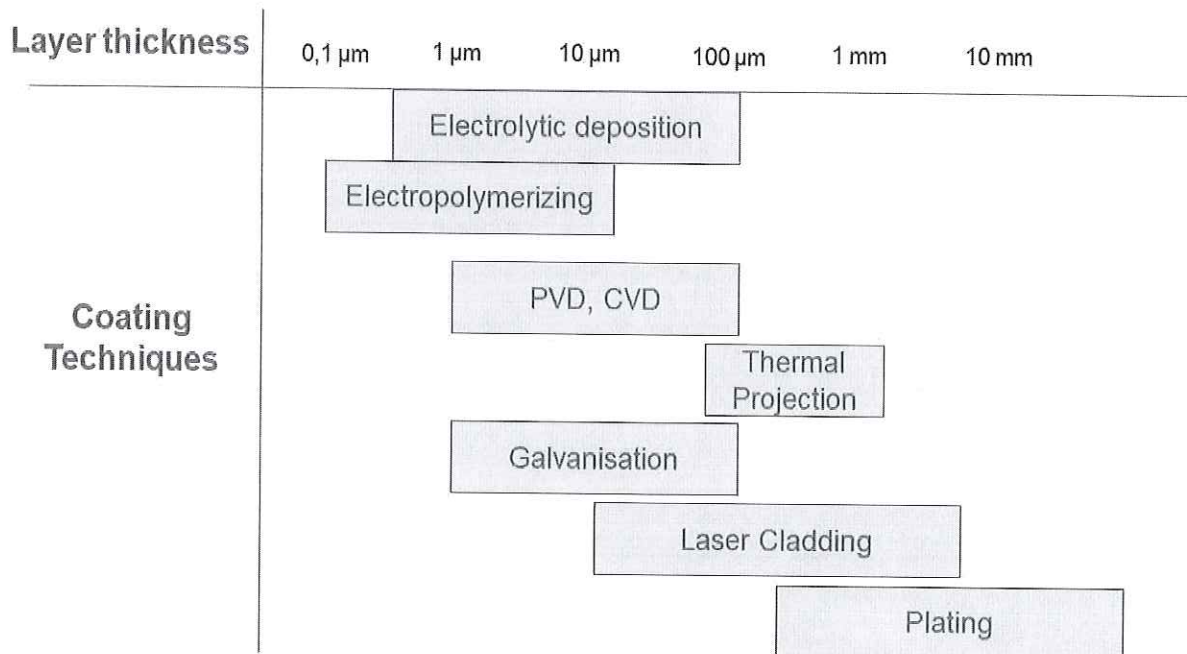
Plating

Coating Techniques

Figure 13: Coating thickness of the most common coating techniques

Every technique has its advantages and drawbacks, and each one is privileged in some sectors even if some of them such as the thermal spraying techniques, are widely used. They are mainly used to bring properties as corrosion protection or thermal protection, even if a wide range of materials can be sprayed with many desired properties. There are some sectors that privilege this technology such as [19, 20]:

Aircraft - for engine manufacture

The goal is to protect the engine from adhesive wear or corrosion, or to protect some part of the engine from the high temperature by making a duplex thermal barrier.

Automobile - for engine manufacture and exhaust pipe

It allows to protect the pipe from oxidation at high temperature, and also allow to extend the engine life by enhancing their mechanical properties.

Food processing industry

In an industry where the cans and containers interact directly with the food, it is necessary to have some precautions as having antitoxic and corrosion resistant coating in the inside of the metallic containers.

Other sectors use this technology as well, to improve their product properties like for example the communication and electronics sector, the chemical industry, the ceramic industry. In addition, thermal spraying can be used in the development of biocoatings for the field of medicine.

2. Thermal spraying techniques

Among all the coating techniques that can be used, there is the thermal spraying, which are widely used to apply, for instance ceramic coatings on metallic or non-metallic substrates. Thermal spray is a group of coating processes used to apply coatings on a substrate by a heating source. Thermal spraying can be divided into three major categories defined by the heating source: **flame spray, electric arc spray,** and **plasma arc spray presented** in figure 14 [20].

Each one of these subsets has its own characteristics. These different energy sources are used to heat the coating material to a molten or semi-molten state. The heated particles are accelerated and sprayed toward a prepared surface by different kinds of jets.
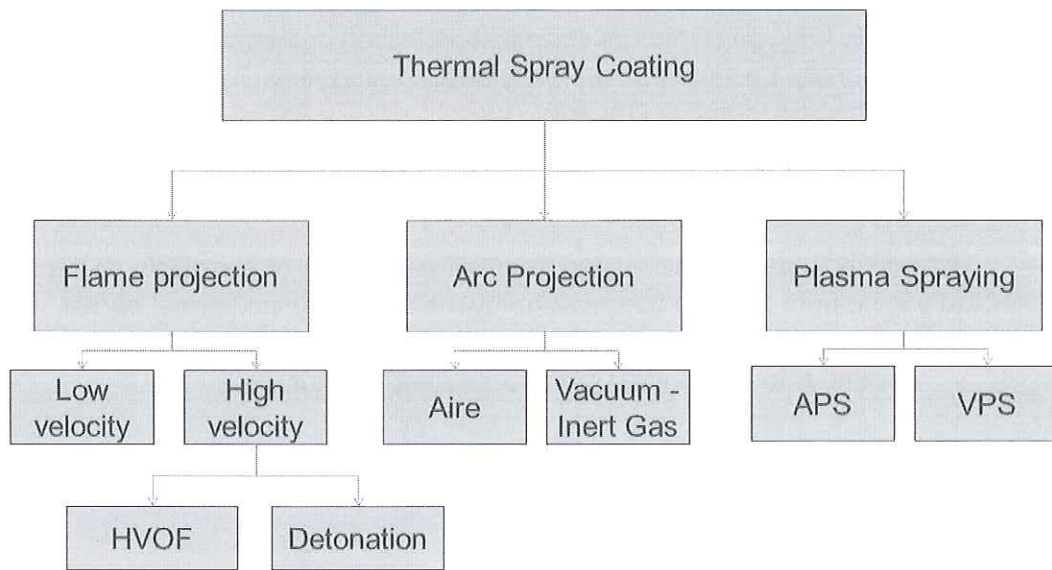
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                    ┌─────────────────────────────┐
                    │    Thermal Spray Coating    │
                    └─────────────────────────────┘
          ┌───────────────────┼─────────────────────┐
┌──────────────────┐ ┌──────────────────┐ ┌──────────────────┐
│ Flame projection │ │  Arc Projection  │ │ Plasma Spraying  │
└──────────────────┘ └──────────────────┘ └──────────────────┘
    ┌──────┴──────┐      ┌──────┴──────┐      ┌──────┴──────┐
┌────────┐ ┌────────┐ ┌──────┐ ┌──────────┐ ┌──────┐ ┌──────┐
│  Low   │ │  High  │ │ Aire │ │ Vacuum - │ │ APS  │ │ VPS  │
│velocity│ │velocity│ │      │ │Inert Gas │ │      │ │      │
└────────┘ └────────┘ └──────┘ └──────────┘ └──────┘ └──────┘
       ┌──────┴──────┐
  ┌────────┐ ┌────────────┐
  │  HVOF  │ │ Detonation │
  └────────┘ └────────────┘
```

Figure 14: Classification of thermal spray coating technique with energy sources

2.1 Spraying by flame

The flame spraying, is the first used technique, developed by a Swiss engineer in 1917. It was first intended to low-melting metals, and then was extended to more refractory metals and ceramics [14].

This technique uses a fuel mixed with an oxidizing agent to provide the energy necessary to melt and accelerate the material via a flame. The flame temperature can be from 3000 to 3350 K. the stand-off distance can vary from 120 to 250 mm. The feedstock material can be in a powder form or a wire. Generally, this technique provides a coating thickness between 100 to 2500 μm with a porosity of 10 to 20% [14].

This family can be divided into two groups in terms of the speed at which the material is sprayed. On the one hand, the low speed technique is the spraying by combustion of powder (material in pulverulent form) or threads (the material is in the form of wire). The material is injected and melted into a flame generated by the combustion inside the gun and it is accelerated towards the substrate by jets of pressurized air.

On the other hand, the high-speed techniques are the spraying by combustion at High Velocity Oxy-Fuel (HVOF) and spraying by detonation. In the HVOF spraying, the material is introduced at the exit of the combustion chamber and both the molten drops and the combustion gases are accelerated through the nozzles inside the gun. In the case of spraying by detonation, the material is introduced directly into the combustion chamber, where a gaseous fuel is ignited and a detonation occurs. This detonation is responsible for melting and accelerating the material towards the substrate.

2.2 Plasma Spraying

The plasma spraying is used since 1960. The heating is produced by the ionisation of a mixture of plasma gases such as H_2, Ar or He. That gases move through an electric arc, and expand forming a jet. The employed feedstock can be powders, suspensions or solutions [17, 19].

The spraying by plasma can also be divided into two groups: atmospheric plasma spraying (APS), and Vacuum Plasma Spraying. In the APS, the atmosphere where the spraying is carried out is air. For the VPS, the spraying needs to take place inside of a vacuum chamber. This is done in order to avoid the decomposition or oxidation of the feedstock material. For both techniques, the material is melt and accelerated by the plasma jet [14].

This technique can go until temperature of 14 000 K, the stand-off distance can be chosen in the range of 60 to 130 µm and the coatings obtained by this technique may have a thickness of 300 to 1500 µm with a porosity of 1 to 7%.

2.3 Spraying by Arc

The spraying by electric arc consists in the use of two wires of the material to be sprayed, loaded with opposite sign to give rise to an electric arc. The high temperature of this arc melts the end of the wires, forming the drops of material that will form the coating. Injecting gas atomizes and accelerates the molten drops and drives them against the substrate [14].

This technique can only be used with conductor wire of a thickness of 1.6 to 5.0 mm, to produce the electric arc. The electric arc spraying may be carried out either in the normal atmosphere of air, in inert gas, or in a vacuum chamber.

The arc temperature can be until 6100 K, the spray distance ranged between 50 and 170 mm, and the obtained coating has a thickness of 100 to 2000 µm with a porosity of 10 to 20% [1].

These techniques have been summarized in a schema (figure 15) [14]. They produce the same parts with the material melting and the accelerating that leads to an impact with the substrate.
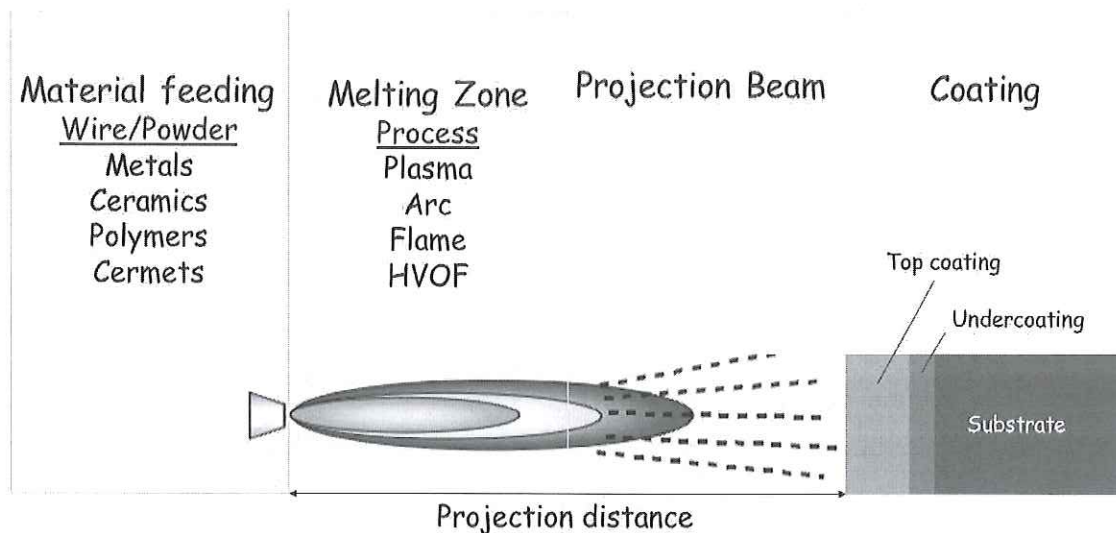
Figure 15: Thermal spaying techniques

3. Plasma spray (APS)

One of the thermal spray coating techniques for the deposition of ceramic coatings is the plasma spray. This leads in general to the formation of amorphous splats which is a necessity in the bioactive glass manufacturing [21].

3.1 Sample preparation

Before coatings deposition [21], it is necessary to prepare the samples in order to obtain the best coating. Therefore, every coating needs a specific preparation. Depending on what coating technique is chosen, the surface preparation is different. For example, for techniques as PVD, that gives very thin layers, the coating will have the same texture than the substrate surface. If the final surface needs to be bright, the sample has to be polished until obtaining a shiny and smooth surface state before the coating.

For thermal spray techniques, as plasma spraying, where the adherence is mechanical, the samples surfaces must possess a certain roughness [14]. To do so, the samples needs to be activated and this can be done with an abrasive blasting, employing water-jet treatment, corundum grit-blasting, laser ablation or chemical attacks.

The commonly used method is grit-blasting with corundum. To achieve the desired roughness, it is important to choose the right blasting grit size. Surface roughness is a parameter which is closely related to blasting. It strongly influences the adhesion of the coating to the substrate. The expected thickness of the coating layer depends directly on the roughness, which is function of the grit size, as explained in table 3 [14].

After the blasting, the samples are cleaned with acetone or ethanol in an ultrasounds tube, to remove any residue and to degrease them.

Table 3: Recommendations concerning the grit sizes used in surface roughening

Grit	Grit size (µm)	Application
Coarse	600 – 2000	Coatings thicker than 250 µm – best adherence
Medium	425 – 1400	Coatings thinner than 250 µm – Fair adherence and smooth finishing surface
Fine	180 – 600	Coatings thinner than 250 µm – not for finishing layers

3.2 Atmospheric plasma torch

The atmospheric plasma spraying is carried out, as in any other method of thermal spraying, by a torch. The schematic section of the plasma torch, presented in Figure 16 [14], shows the main parts such as a circular anode generally made of copper and a cathode of thoriated tungsten or of graphite.

An electric arc produced by the generator through the connectors, heats the working gases, which leads to form a jet. The material that needs to be sprayed as a suspension, solid or liquid form is directed in the centre of the flame. It first melts, then it is accelerated in the jet and finally impacts the substrate. The adherence of the coating is mechanical; therefore, the surface preparation is very important as mentioned above [14].

Among the plasma torch parameters, there are the gases used to produce the plasma rate. It is possible to use argon or mixtures of argon and hydrogen, argon and helium or argon and nitrogen. Every gas has a role. In fact, Ar stabilizes the arc inside a nozzle, He, N_2 or H_2 enhance the heat transfer to the particles, due to their high heat conductivity. The most used is the mix between Ar and H_2.
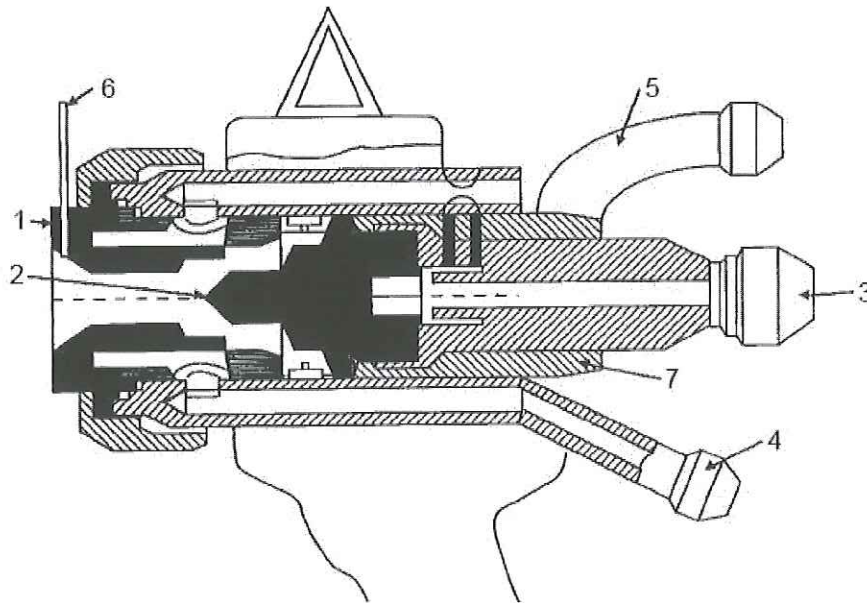
Figure 16: Schema of a section of plasma torch: (1) anode, (2) cathode, (3) water outlet and cathode connector, (4) water inlet and anode connector, (5) inlet for working gases, (6) powder injector, (7) electrical insulator

The arc produced depends on the electric current and the voltage. The first one is about a few hundreds of amperes and the second can vary with the distance between the anode and the cathode and the choice of the second gas.

The plasma torch is installed on a robot arm and it is controlled with a computational programme. This allows to do the coatings with a precision and a reproducibility more significant than with other thermal spraying techniques, where the gun is held by an operator such as the flame spraying [14].

3.3 APS feedstock

The commonly sprayed material in APS are powder feedstocks. The grain size distribution is an important parameter. It can be injected in two ways: inside or outside the anode nozzle. The injection inside the nozzle make the trajectory of the particle in the jet longer. This enable to use less power to spray, but the torch needs to be cleaned more often. The exterior injector is generally placed to distribute the powder with an angle of 90° [14].

The inert gas (Ar) that distributes the powder, is usually around a rate of 4-6 slpm (standard litre per minute). In figure 17 [14] there is an example of a powder feeder, which can deliver two powders simultaneously. It distributes the powder on a rotating wheel with an orifice. The powder feed rate, controlled by the disc rotational speed usually, it is about 10 to 150 g/min.
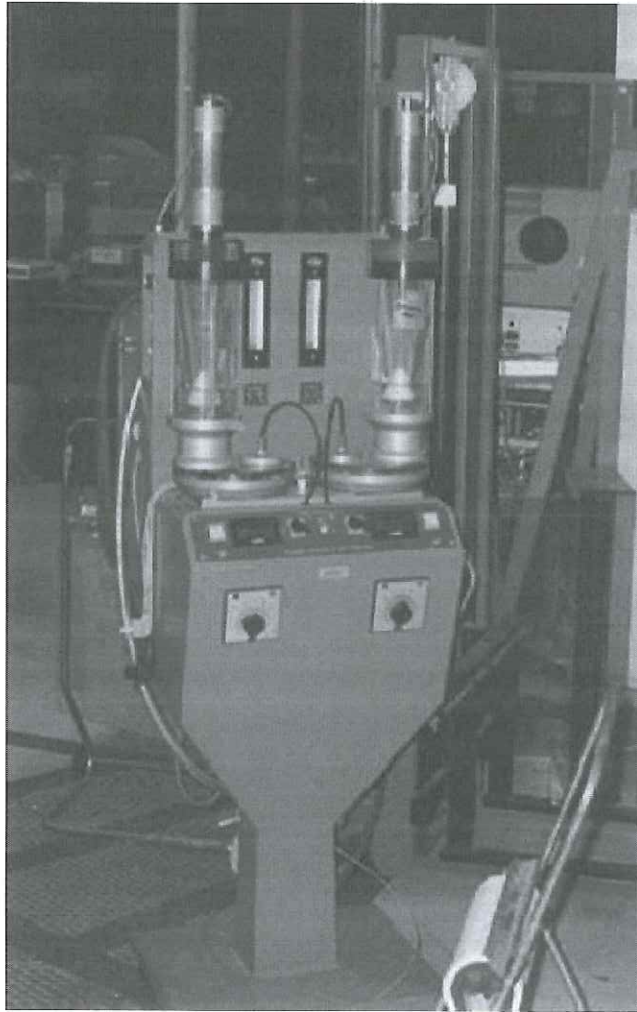
Figure 17: A double powder feeder for APS

3.4 Coating build-up

The plasma jet propelled the material against the substrate. Thanks to the impact, a mechanical bond is formed with the surface. The molten particles form a lamellar structure (figure 20) [14] called "splats". The particles can be fully or partially melt, or on the other hand it can also be totally solid due to an excessive time of residence into the plasma torch or a higher particle size. This fact gives a poor adherence and mechanical properties. However, this non-desired kind of particles must be avoided by the properly choice of the spraying parameters.

During spraying, first, the molten particles are propelled on the substrate thanks to the plasma jet. Then they are progressively deformed until becoming lamellar splats. A layer, considered as the coating after one pass of the spaying torch, can be formed from 5 to 15 lamellae. The number of splats per pass depends on the torch parameters as the velocity, the distance of spraying and the material feeding rate. During every pass, the cooling can induce additional stress to the coating. This kind of stress can also be because of the re-heat of the

31

previously deposited material. The final layer is very important to the whole coating adherence, indeed because of the thermal stress, the coating can be detached from the substrate at the end of the spraying [14].
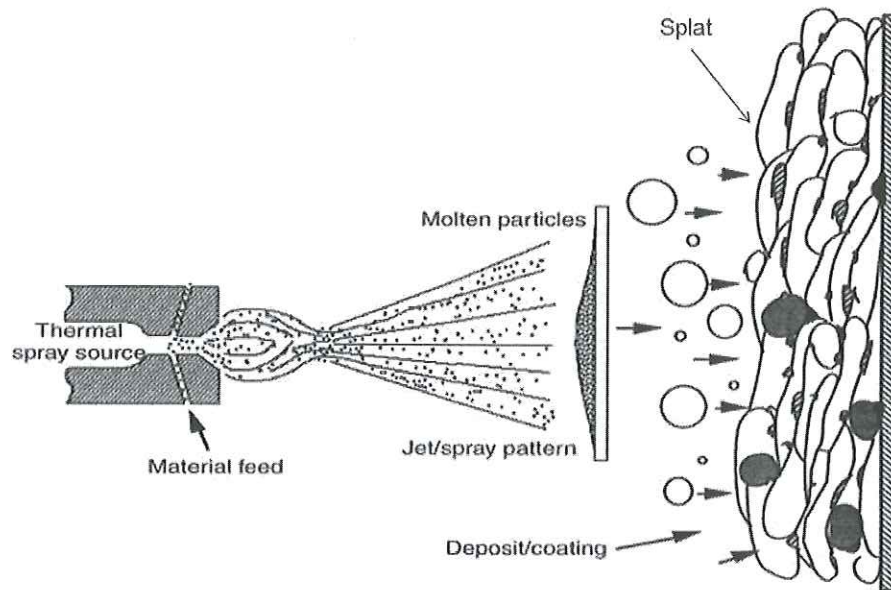

Figure 20: A typical plasma spray process and coating

3.5 Solution Precursor Plasma spraying

Concerning APS, suspensions and solutions can also be sprayed instead of powders. These techniques are known as Suspension Plasma Spraying (SPS) and Solution Precursor Plasma Spraying (SPPS). The use of liquid feedstocks is a technical key for obtaining coatings with fine microstructures, since spraying fine powders is not an appropriate way to obtain such coatings [19, 22]. This is due to the fact that powders with a particle size of 5 to 10 μm or finer cannot be transported due to their poor flowability. To overcome this drawback, the fine powders can be injected into the torch as a suspension. However, it is also possible to employ a solution of precursors, obtaining coatings with an improved microstructure compared to those obtained by APS or SPS [14]. SPPS method, is based on the deposition of solutions, developed by the sol-gel method, before the gelation and after being aged at a characteristic period of time.

The coatings done using liquid feedstocks have much finer surfaces than the coatings spayed using powders. They are also thinner and need more energy to be sprayed because a large amount of the energy used to evaporate the liquid. This technique is used to obtain nano-structured coatings. Moreover, this technique can avoid doing a post-mechanical treatment since the obtained coating is smooth enough [19].

First the liquid is contained in a container like that presented figure 18 [14]. The liquid feedstock is stored under high pression with compressed air, and is delivered to the torch by a pressure difference. The compressed air need to be under a pressure of 5 to 6 bar. Both types of liquid feedstocks were transported into an atomiser before being injected into the plasma torch, in order to obtain fine droplets of the feedstock. An example of an atomiser is presented in figure 19 [14].
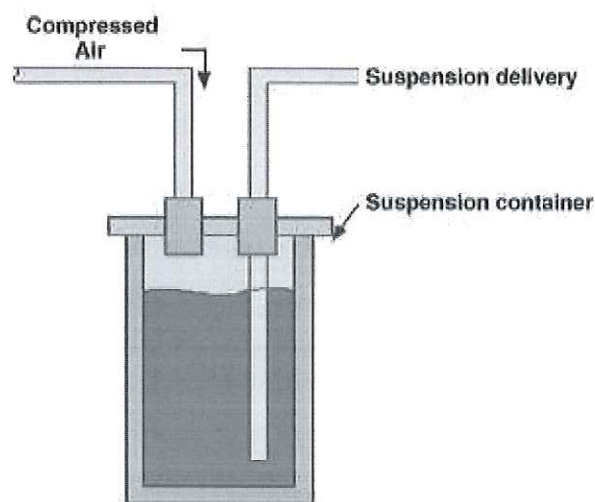

Figure 18: Liquid container for Solution Precursor Plasma Spraying

While in the jet, the liquid feedstock suffers some chemical transformations, which are function of the type of liquid feedstock. In the case of suspensions [19], the droplets break

aerodynamically, then the solvent evaporates and after that the fine solid particles coalesce between them. When solutions are used [22], after the droplets breakup, takes place the solvent evaporation, gelation step, breakup of the gel, the pyrolysis of the gel particles and the formation of solid particles. From this point, the steps in the flame are the same as in the case of powder feedstocks. The just formed solid compound is melt and accelerated by the jet, and it is propelled on the substrate.

Concerning the spraying parameters, both enthalpy and the sand-off distance are the most critical instead the others. A more energetic torch is needed in order to evaporate the solvent and melt the particles while short distances are needed in order to avoid the solid particles volatilisation due to the high energy of the torch [22].

Regarding biocoatings, SPPS represents a well method to deposit this type of coatings since this technique has the capacity to melt ceramic particles and gives thin coatings. SPPS is employed in the literature for the deposition of calcium phosphate coatings such as hydroxyapatite, but there are few studies related on the deposition of bioactive glasses by SPPS. Therefore, the present work represents a novel study of bioactive glass coatings deposited by thermal spraying.
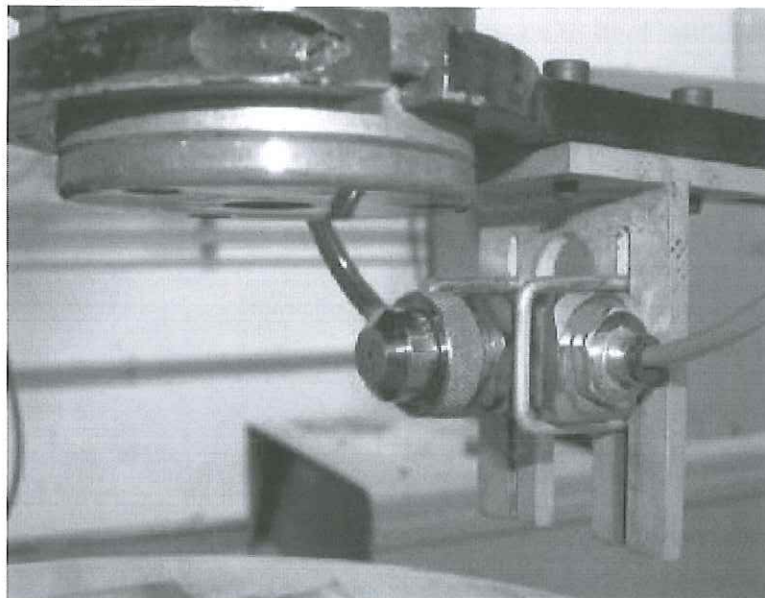
Figure 19: A liquid atomizer attached to a commercial plasma torch

II.   Goals of this study

This study has been conducted to pursuit a previous work that dealt with 45S5 bioactive glass coatings deposited by plasma spraying from powders and suspensions as feed materials. The sprayed material was made by casting and crushing and then obtaining the frit. The results of the first study gave coating with large particles. The plasma spraying lead to aggregation and partially un-melted splats. In order improve the properties of the coating, it would be better obtaining a finer microstructure. To do so the idea is to spray a solution of the same composition of the employed feedstocks. The solution will be prepared via the sol-gel technique and spray it thanks to the air plasma spraying before it jellifies. The solution will contain colloidal particle and while sprayed shall gave a finer microstructure.

This study will be based on obtaining the best bioactive glass coating. Many parameters need to be taken into account in the solution preparation such as the time of gelation, the amount of catalyst, but also in the thermal spraying technique, like for example the stand-off distance or the torch's enthalpy.

To complete this study, preliminary coatings were sprayed, testing of all these parameters to find the optimal spraying parameters. The tests will be done on steel samples with a bond coat of titania. To found the depends of the different parameters a design of experiments will be developed, taking into account the more important parameters.

Furthermore, it would be interesting to characterise the obtained solution, measuring it viscosity and gelation time, but also the powder obtained by drying the solution. Finally, the obtained coating was characterised.

III. Experimental process

A. The solution feedstock synthesis

In the present work, concentrated solutions (4M) with a composition close to the 45S5 bioactive glass were used as feedstocks. The precursors employed are described below:

- TEOS (Tetraethyl orthosilicate, MERCK, Germany) as SiO_2 source.
- TEP (Triethyl phosphate, MERCK, Germany) as P_2O_5 source.
- $Ca(NO_3)_2$ (Calcium nitrat-Tetrahydrat, VWR, Belgium) as CaO source.
- $NaNO_3$ (Sodium nitrate, SIGMA-ALDRICH, Japan) as Na_2O source.

Solutions were prepared employing different catalyst concentrations (0, 0.2, 0.5 and 1M). As catalyst, nitric acid (Nitric Acid 10M, MERCK, Germany) was chosen, since it is well studied in the literature in the development of bioactive glasses by the sol-gel method. The methodology followed to prepare the solutions is shown in figure 21.
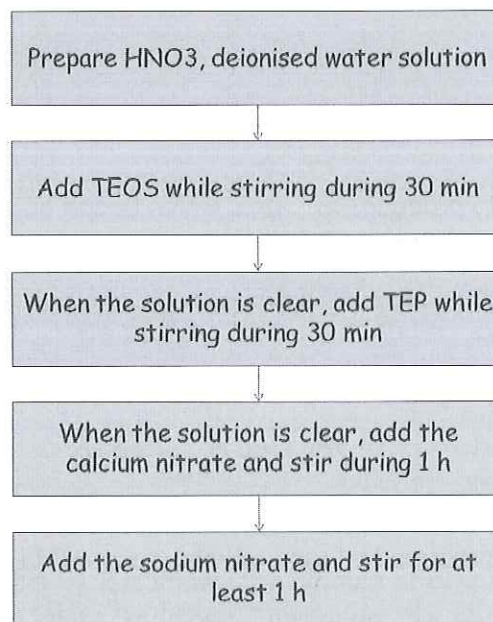

Figure 21: Chart of the solution preparation

First, nitric acid was added to the water in order to obtain a dissolution with the desired concentration of catalyst. Then the TEOS was added and stirred during 30 minutes until the solution has become clear. Then, TEP was added with the same procedure as in TEOS addition. When the solution was again completely clear, the calcium nitrate powders were added progressively and stirred until its complete dissolution (1 hour approximately). After that, sodium nitrate was added following the same procedure used with the calcium nitrate powders. Every preparation step is done under a chemical extractor hood with a continuous magnetic stirring.

B. Feedstocks characterisation

In order to know the materials properties, both the powders (with the selected catalyst concentrations) and the coatings were characterised [23].

1. Chemical analysis

The powder is first characterized by XRF to know their composition. The X-ray fluorescence is a non-destructive technique that uses X-rays to determine the chemical composition. This method is based on the principle of absorption of X-rays by the material. The material atomic excitation leads to the release of an X-ray fluorescence. Indeed, the X-ray incident dislocate an electron from the intern layer of atoms, one other electron takes the vacant site and in the meantime, there is a liberation of energy as x-ray fluorescence as explained in figure 24 [24].

Since every chemical element has a characteristic response to this excitation, a qualitative analysis can be easily done. To obtain a quantitative analysis is however possible by comparing the results to a patterns sample, to establish the proportion of element present.
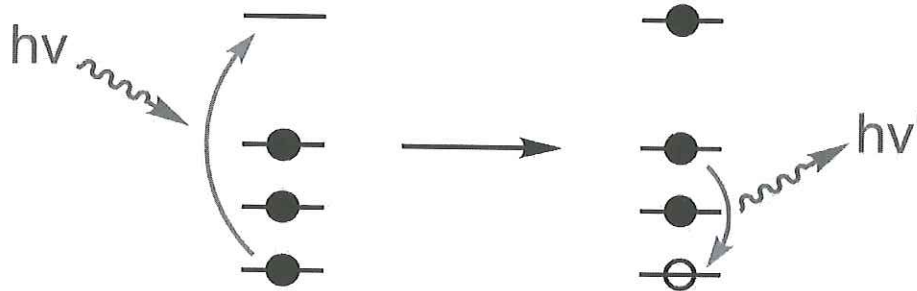

Figure 24: Schema of the x-ray fluorescence

2. Particles size distribution

Then powders are characterised by laser diffraction method to obtain the particles size distribution. The laser beam passes through a dispersion of particles in a liquid. The results are collected as the diffraction of the laser beam. The angle of diffraction increases when the particle size decreases. This technique is usually used to measure particles size between 0.1 and 3000 µm. The final result is given as a size distribution curve.

3. X-Rays Diffraction

The X-rays diffraction is a characterisation technique that allows to know the material crystalline structure. Indeed, this method use a beam of X-rays that, when the material has a crystalline lattice, diffracts in specific direction with different angles and intensities according to the crystalline structure. The diffractometer used is the advance diffractometer (Bruker Theta–Theta, Germany).

To characterise a powder, it needs to be prepared carefully to have a plane surface avoiding any privileged plan. To do this, the powder needs to be crunched into a mortar and then put into the sample holder, and its surface is smoothed with a glass lamella.

4. Scanning Electron Microscopy

The Scanning Electron Microscopy (SEM) is a technique that allows to characterise the surface topography. A beam of electrons, focused by magnetic lenses scans the surface, other electrons are emitted and collected by the detectors. The number of secondary electrons detected helps to form a high-resolution image.

In order to avoid an accumulation of electron on the non-conductive powder, the powder undergoes a flash of gold.

5. Thermal characterisation

The thermogravimetric analysis (TGA) and a differential Thermal Analysis (DTA) allow to see how the material will act once in the plasma jet.

First the TGA allows to know the physical and chemical changes that occurs in a material while increasing the temperature with a constant heating rate. These changes are going to be deduced from a curve that shows the variation in the material weight. Weight loss or gain at a precise temperature are going to reveal the kind of transformations that are occurring, such as dehydration, decomposition or oxidation. The material's weight is measured with a micro-balance loaded with material while increasing the temperature.

Then DTA can be done in the same time than the TGA and measures the material's the enthalpy changes. The powder is placed in the centre of the furnace. One holder is filled with the sample and the other with an inert referential material, such as alumina. Thermocouples inserted in each holder measure the temperature difference between the sample and the reference as the temperature of the furnace is controlled by a temperature programmer. This technique will give a curve with exothermic or endothermic changes. The DTA is a complementary method to the TGA, because it confirms the changes deducted with the TGA and it also detects reactions that occur without weight changes.

The analyses (TGA/SDTA 851e, Mettler Toledo, Switzerland) are done using a platinum crucible in air atmosphere by increasing the temperature from 25°C until 1203°C with a heating rate of 10°C/min.

Then the powders are characterised with heating microscopy to understand how its contraction and fusion. The temperature will be increased until 1550°C. This technique will provide the characteristics temperatures and the curve of the contraction of the powder. This method consists on putting a rectangular sample of the powder and measuring it shape with an image analysis technique while increasing regularly the temperature.

C. Plasma spraying

1. Sample preparation

As explained earlier, it is necessary to have a certain roughness while using the plasma spraying technique. The coating will be bonded to the substrate thanks to this roughness. To obtain this mechanical adherence the substrates (AISI type 304) will be blasted with fine black corundum. The blasting machine sprays the grit thanks to pressurized air at 4.2 bar.

The sample is hold by the operator horizontally under the blasting. Surface roughness (Ra) of grit-blasted and cleaned substrates was measured with a roughness tester (HOMMELWERKE T8000, Hommelwerke GmbH, Germany). The roughness was 2.2 ± 0.1 µm. Then the sample is cleaned in ethanol in an ultrasound tube for 3 minutes, to remove any residue.

Then, a titania bond coat is sprayed by APS with the parameters in table 7. A bond coat is needed when the top-coat is very different from the substrate. The goal of the bond coat is to provide intermediate properties to improve the top coat's adherence, because the adherence is higher between similar materials

Table 7: The bond coat spraying parameters

Spray distance	Gases flow rate H_2/Ar	Torch velocity
120 mm	14/38 splm	1000 mm/s

2. Spraying parameters

In the present work, preliminary bioactive coatings were deposited. For that purpose, a plasma torch was employed (F4-MB, Sulzer Metco, Germany), which is managed by a six-axis robot (IRB 1400, ABB, Switzerland). The plasma gases used were argon as primary gas and hydrogen as the secondary gas.

There are various parameters that have an influence on the spraying. This study is meant to define which are the optimal parameters. To do so, it is important to understand what parameters can be modified and how they influence the coating results.

Firs, among the spraying parameters, there are some fixed parameters that have been decided and these will not be changed during this work. These parameters were:

- The torch/sample holder velocity (respectively 1250 mm/s and 0.72 mm/s), in order to obtain the equivalent of one pass with the APS.

- The Torch intensity (600 A)

- The number of spray passes (5)

- The solution flow pressurized at 6 bar (maximum pressure)

- The injector/jet distance (a standard distance)

- Pre-heating the sample at 300°C

Then there are the parameters that will be varied until obtaining an optimal coating:

- The spray distance can vary from 60 to 130 mm (influence on the particles melting)

- The work gases flow rate (amount of argon regarding the amount of hydrogen influence the jet enthalpy)

3. Design of experiment

In order to define how every parameter influences the coating adherence a design of experiment is done [25, 26]. To do so three parameters are tested each one with two levels as seen in table 8. Indeed, as parameter A, the stand-off distance will be tested at 70 and 110 mm. then the enthalpy of the jet will be changed with the parameter B. In order to test two levels of the enthalpy, the heating gas (hydrogen) will more or less diluted into argon. Finally, the influence of the catalyst will be taken into account by testing a 0M and 0.2M solutions. To have more significant values, every test is done twice and the mean value will be used in the calculations.

Table 8: Design of experiment parameters

Level	Distance (A)	Gases flow rate (B) H_2/Ar	Amount of catalyst (C)
Low (-1)	70 mm	15/25 splm	0 M
High (1)	110 mm	15/45 splm	0.2 M

The studied property is the adherence of the coating to the substrate. Since it is expected that all coatings have a very thinner thickness, this value cannot be assessed by the ASTM-C633 standard, which is typically employed in thermal sprayed coatings. For that
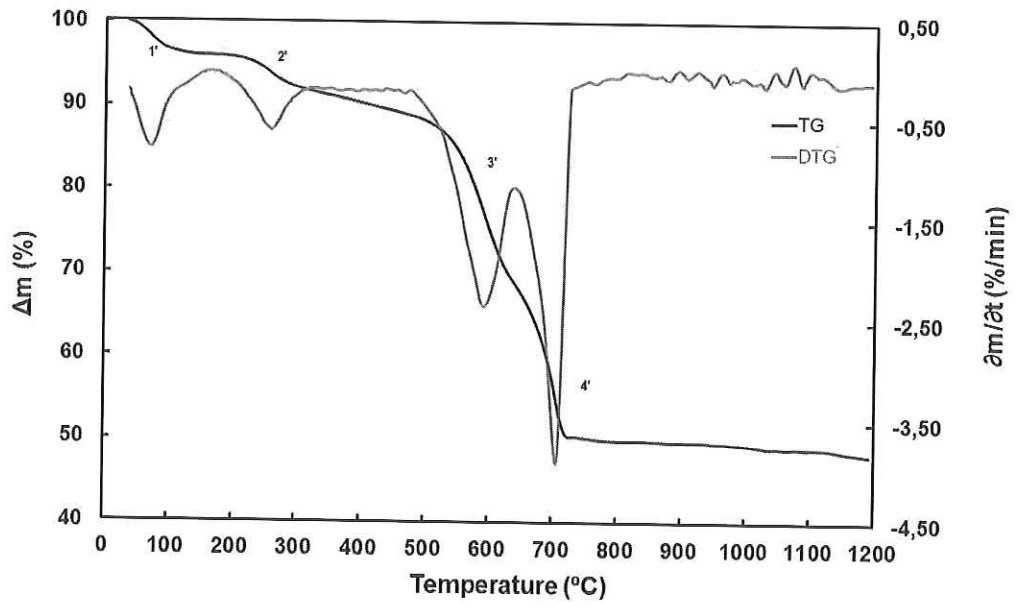
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Figure 29: TGA curve of the bioactive glass dried powder-solution at 0M of nitric acid
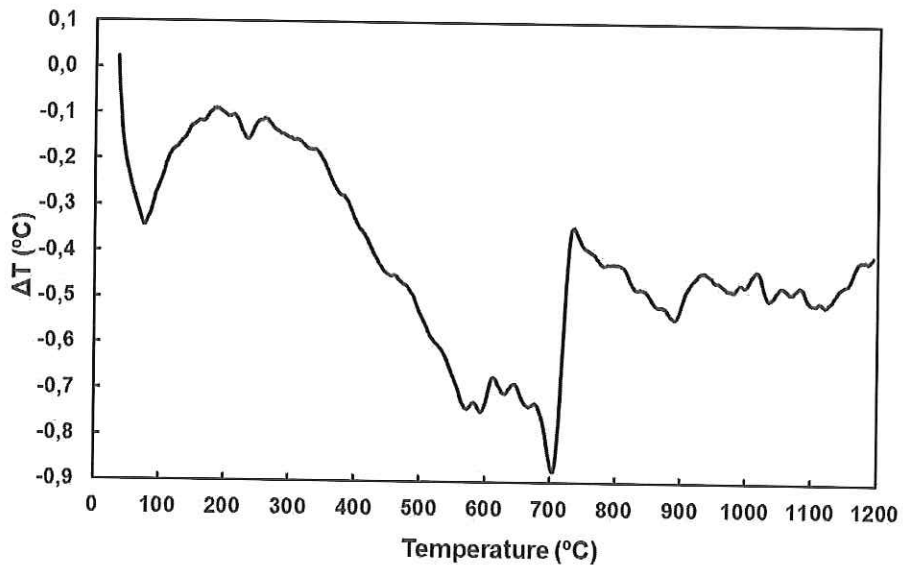

Figure 30: DTA curve of the bioactive glass dried powder-solution at 0M of nitric acid
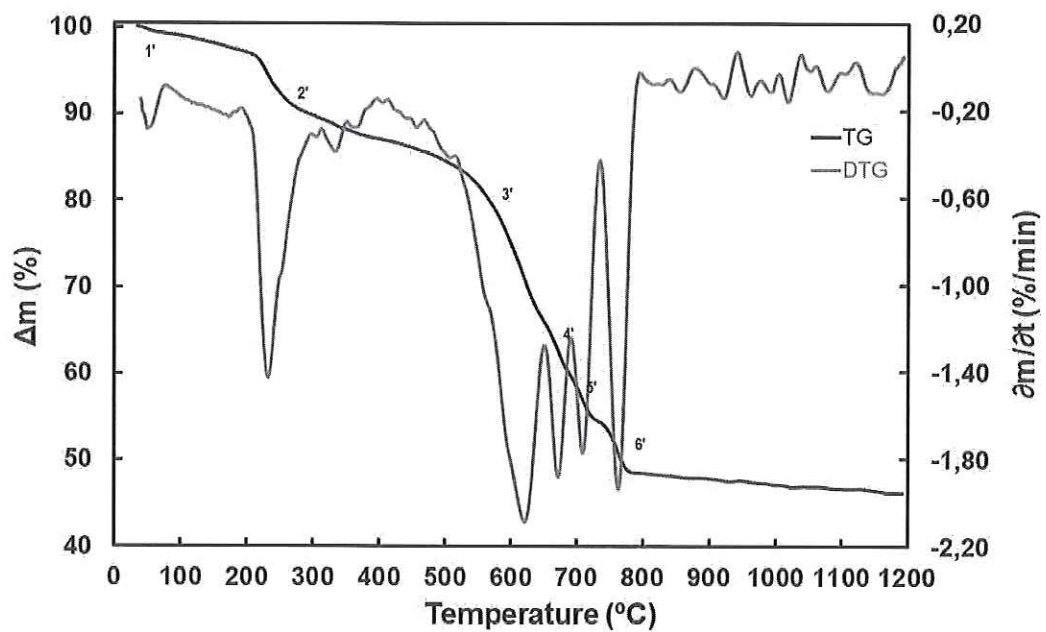
Figure 31: TGA curve of the bioactive glass dried powder-solution at 0.2M of nitric acid
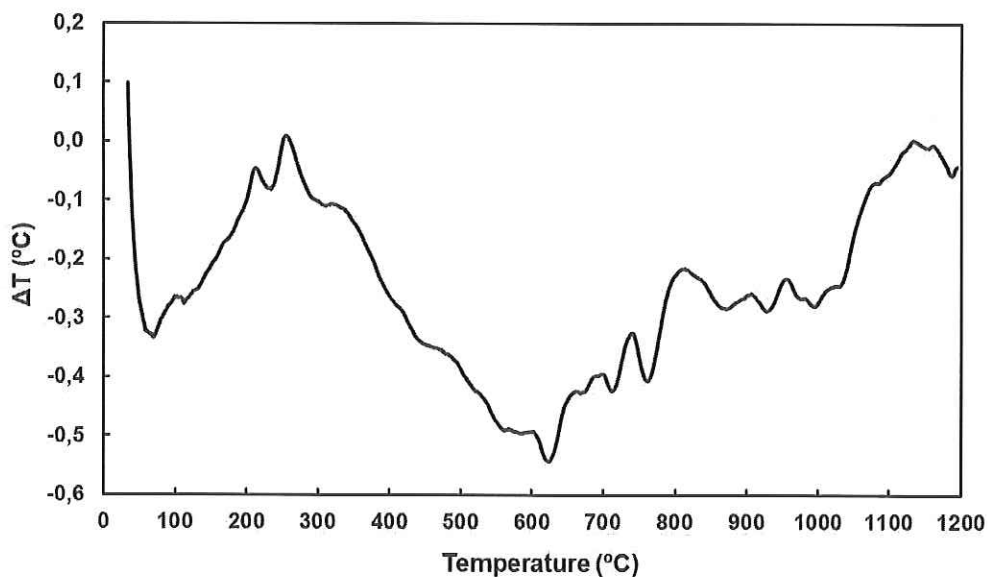

Figure 32: DTA curve of the bioactive glass dried powder-solution at 0.2M of nitric acid

The results of the heating microscopy of the 0M solution are given as: the characteristic temperatures (table 11) and the contraction curve (figure 33). The sphere or a semi-sphere temperature are not given because of the nature of the material. The material melt without taking these shapes. The beginning and final contraction temperatures correspond to the weight loss at same temperature in the TGA results figure 29.

Table 11: Characteristic temperatures of the 0M bioactive glass powder

Characteristic Temperatures	Beginning of contraction (99%)	Final contraction	Softening	Sphere	Semi-sphere	Fusion
SG-0	260	715	1065	-	-	1185

The contraction curve (figure 33) shows a contraction about 10% between 200 and 700°C. This corresponds as seen in the TGA to the evaporation of the nitrate around 200°C, and then the organic compounds around 700°C with an abrupt contraction. The curve shows, between 800 and 1000°C, an absence of contraction that corresponds to the devitrification of $Na_2Ca_2Si_3O_9$ as seen also in the DTA peak at the same temperature [15].

The result of the 0.2M powder are not exploitable because the sample did not act as usual and collapse all at once.
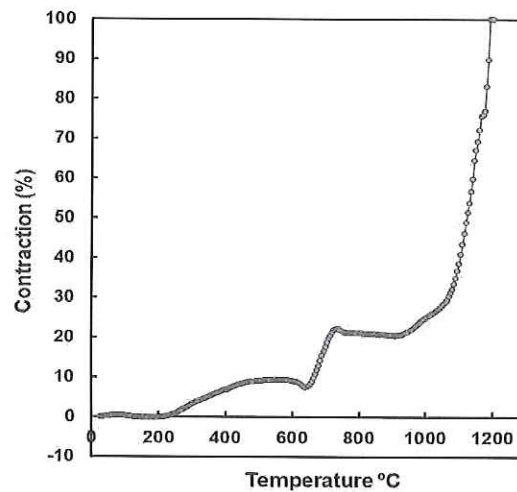

Figure 33: Contraction curve of the 0M bioactive glass powder

1.5 Scanning Electron Microscopy

The results of the observation of the powders with the SEM are shown in figure 34. The 0M powder in fig 34-A has smaller particles than the 0.2M powder, seen in fig 34-B. This result confirms the particles size distribution seen earlier.

Crystallites of $NaNO_3$ can be observed on the particles' surface, as it will be seen in the XRD results figure 35. They are more numerous and larger for the 0.2M powder. Moreover, the 0.2M particles seem more homogenous than the 0M, which is logical regarding the gelation time results and the viscosity results the 0.2M solution has a more advance hydrolysis and condensation reactions.
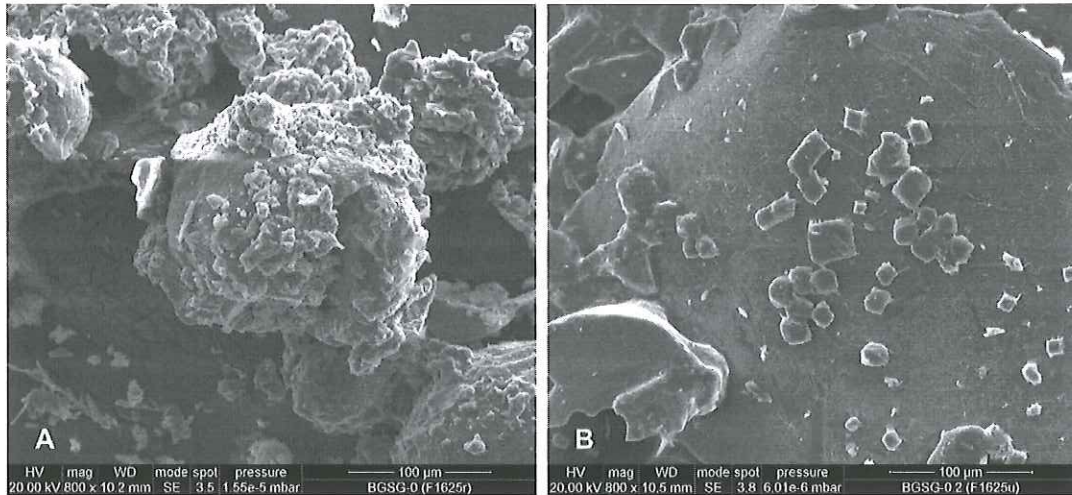
Figure 34: Micrographs of the dried powder (A) 0M of nitric acid, (B) 0.2M of nitric acid

1.6 XRD

In this study, the desired bioactive glass should have a totally amorphous structure. The results (figure 35) shows an amorphous structure except for one peak (at $2\theta = 30$), but this peak of sodium nitrate should disappear after spraying. Indeed, since the dried gel has not been submitted to any thermal treatment, the remain nitrate from the catalyst and the other precursors give this peak. The graph in figure 35, compares the two solution's results. The graphs are similar except for the peak intensity, which is higher for the solution with the catalyst since it contains more nitrate and the particles are bigger than in the 0M solution.
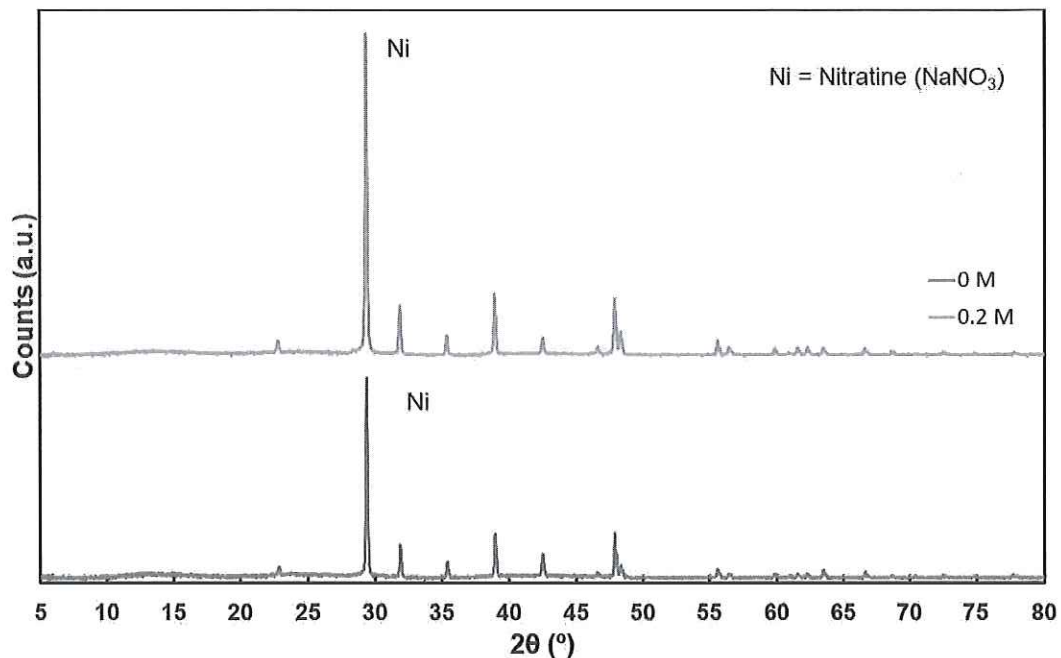

Figure 35: XRD results for the bioactive glass dried gel with 0M and 0.2M of nitric acid

The graphic shows the same XRD shape for the two concentrations, with very few peaks. The larger peak is identified as "Nitratine", a crystalline form of sodium nitrate, that is present because the material did not been sintered yet. This is the only peak that is more intense for the higher concentration, probably because there is also diffraction from the nitrate of the catalyst. Otherwise this chart shows an amorphous material

2. The design of experiment results

The eight tests done varying every time one parameter have given coating with various adherences, as seen in figure 36. The results of every adherence are given for both tests in table 12.
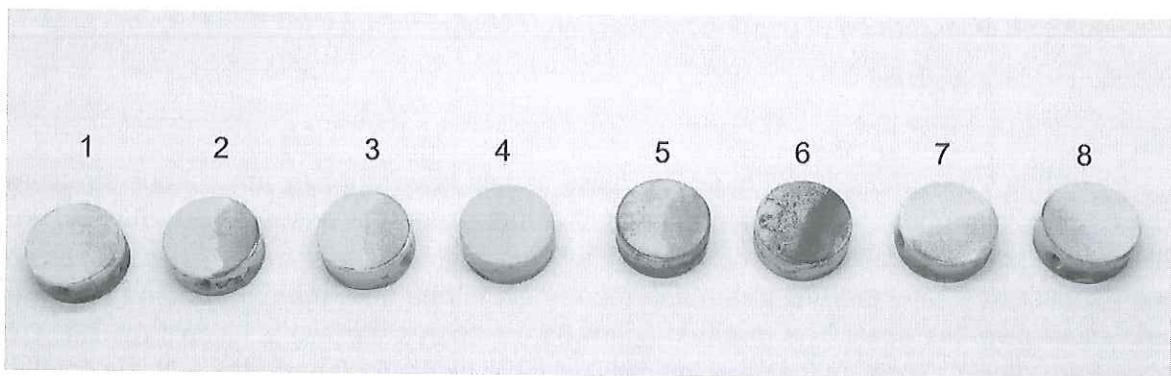

Figure 36: Coatings results

Table 12: The adherence results of the design of experiment

Combinations	Factorial effect							Adherence scale	
	A	B	C	AB	AC	BC	ABC	Test 1	Test 2
1	-1	-1	-1	1	1	1	-1	3.0	3.0
2	1	-1	-1	-1	-1	1	1	2.0	3.0
3	-1	1	-1	-1	1	-1	1	1.0	1.0
4	1	1	-1	1	-1	-1	-1	2.0	1.0
5	-1	-1	1	1	-1	-1	1	4.0	4.0
6	1	-1	1	-1	1	-1	-1	2.0	3.0
7	-1	1	1	-1	-1	1	-1	2.0	2.0
8	1	1	1	1	1	1	1	3.0	2.0

In order to know the influence qualitatively, the contrast is calculated. This value is equal to the adherence scale pondered with every parameter's vector. Then this value leads to the effect of every parameter.

The effect is defined, in eq. 11, as:

$$Effect = \frac{Contraste}{n2^{k-1}}$$

(Eq. 11)

With **n = number of properties** (here 1)

and **k = number of parameters** (here 3)

The results are shown table 13. It seems like the parameters that have a high influence on the adherence are the B (gases flow rate) and C (the catalyst concentration) and the interaction AB (both stand-off distance and the gases flow rate). In tables 13 and 14, the parameters with the higher absolute value of effect are highlighted in yellow, because they will be those that have the more influence on the adherence.

Table 13: Qualitative results of parameters influence

Variable	Contrast	Effect
b0	-	2.375
A	-2.00	-0.25
B	-10.00	-1.25
C	6.00	0.75
AB	6.00	0.75
AC	-2.00	-0.25
BC	2.00	0.25
ABC	2.00	0.25

A variance analyse is done to confirm the results obtained by calculation of the effect. It will lead to know the probability of influence of every parameter. The parameters with more influence are those which have at least 95% degree of certainty (highlighted in table 14).

Table 14: Quantitative results of parameters influence

Variable	Con-trast	SS	gl	CM	Fo	Ft	P	Signif.
						α = 0.05		
A	-2.00	0.25	1.00	0.25	0.89	5.32	37.34%	62.66%
B	-10.00	6.25	1.00	6.25	22.22	5.32	0.15%	99.85%
C	6.00	2.25	1.00	2.25	8.00	5.32	2.22%	97.78%
AB	6.00	2.25	1.00	2.25	8.00	5.32	2.22%	97.78%
AC	-2.00	0.25	1.00	0.25	0.89	5.32	37.34%	62.66%
BC	2.00	0.25	1.00	0.25	0.89	5.32	37.34%	62.66%
ABC	2.00	0.25	1.00	0.25	0.89	5.32	37.34%	62.66%
Error	-	2.25	8.00	0.28	-	-	-	-
Total	-	13.75	15.00	0.92	-	-	-	-

In table14, that gives the same results than the values given table 13. These values are used to build a model that will predict the adherence. An equation of parameters' influence over the adherence can be elaborated thanks to this data (Eq. 12):

$$Y = 2.37 - 0.125A - 0.625B + 0.375C + 0.375AB \quad \text{(Eq. 12)}$$

The parameter A (the stand-off distance) is not significative because it only got 62.66%, but since it appears in the interaction AB, it must be taken into account.

This equation (Eq. 12) is logical with the empirical tests. Thanks to these tests, the optimal coating parameters seem to be those for the sample n°4, that have a very good adherence. The parameters of this coatings are the spraying of 0.2 M solution at a distance of 70 mm, and an enthalpy of 15/25 slpm.

3. The coating characterisation

Since the sample n°4 is the only one with good adherence, it is the one that have been observed in section with the SEM and characterised by XRD. Indeed, if the adherence is not good enough, the coating will be ripped off by the water during the cutting.

The surface scanning does not need metallographic preparation, the coating with a good adherence will be compared to a sample with poor adherence.

3.1 SEM

The scanning Electron microscope show in fig 37 and 38 the morphology of the coating surface of two sample. The fist fig 37 has a poor adherence, which can be associated to the circular shape of the particles. Indeed, this could significate that the particles have been molten but they have had the time to solidification before reaching the substrate. In this case the stand-off distance (110 mm) is too long.
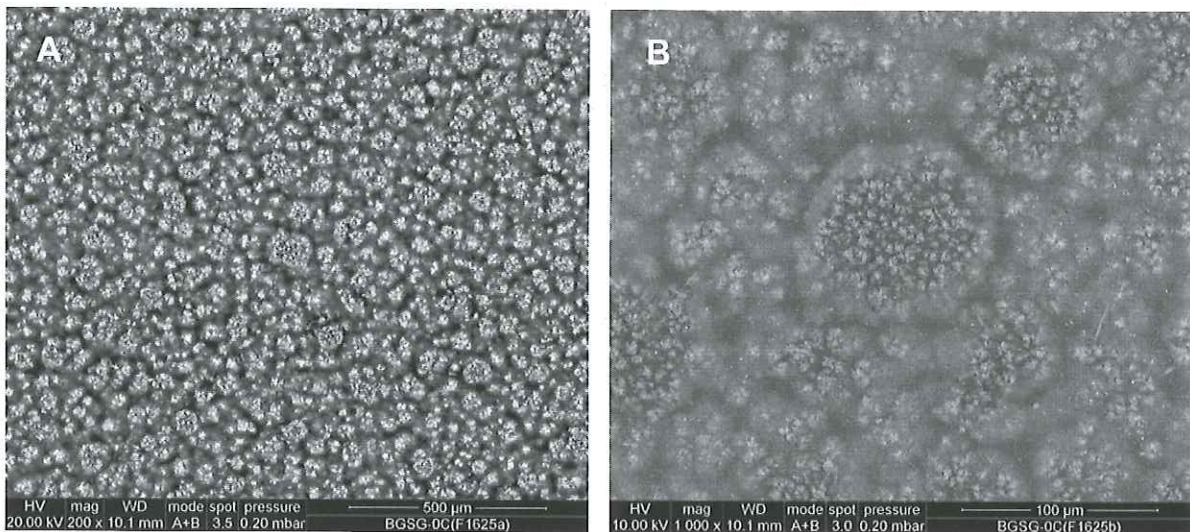

Figure 37: Micrographs of the surface of bioactive glass at 0M nitric acid, sprayed at 110 mm with an enthalpy of 15 Ar-45 H₂, (A) X200 (B) X1000

The second substrate has a better adherence. The more molten state of its surface shown in fig 38(B) indicates that the stand-off distance is more appropriate. The particles seem agglomerated but some of them seem very small. This coating seems denser than the first one but it is still porous. This open porosity is an advantage in this case because it increases the bioactive glass specific area, and so does its reactivity in the SBF.
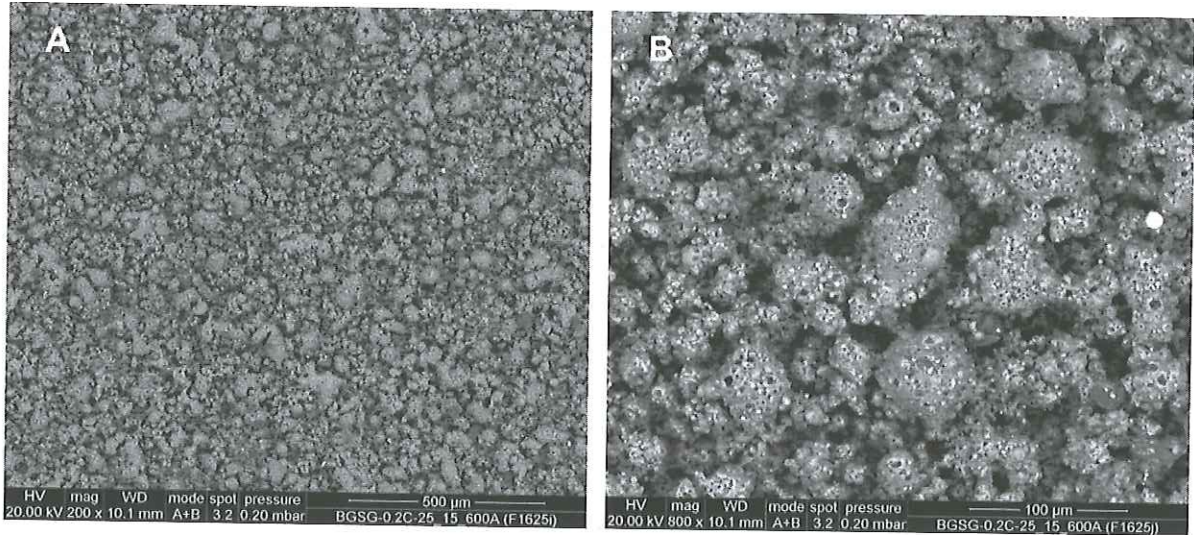
Figure 38: Micrographs of the surface of bioactive glass at 0.2M nitric acid, sprayed at 70 mm with an enthalpy of 15 Ar - 25H₂, (A) X200 (B) X800

The SEM section micrograph (fig 39) shows clearly the characteristic splats. Some intern porosity can also be seen. In the micrograph fig 38-B, the bioactive glass as top coat is filling the roughness of the titania bond coat as expected. The surface seems smooth which means that the particles have a fine size. In figure 39-B, the top coat is about 30 µm, which can be sufficient for its use.
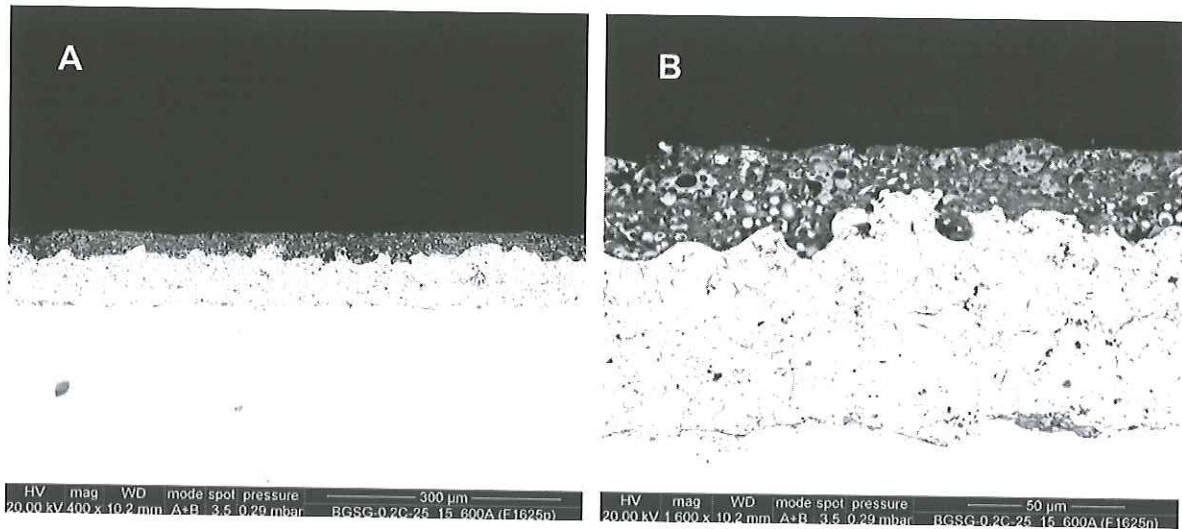

Figure 39: Micrographs of the section of bioactive glass at 0.2M nitric acid, sprayed at 70 mm with an enthalpy of 15 Ar- 25H₂

3.2 XRD

The coating with good adherence was characterised by the X-ray diffraction to see its crystallinity. As shown in figure 40, obtained coating is totally amorphous.

Moreover, the crystallized $NaNO_3$ present in the dried sol-gel has also disappeared, due to the high temperature reached in plasma jet responsible for the melting but also the high-velocity impact that leads to a very rapid cooling that forbid any crystallisation.
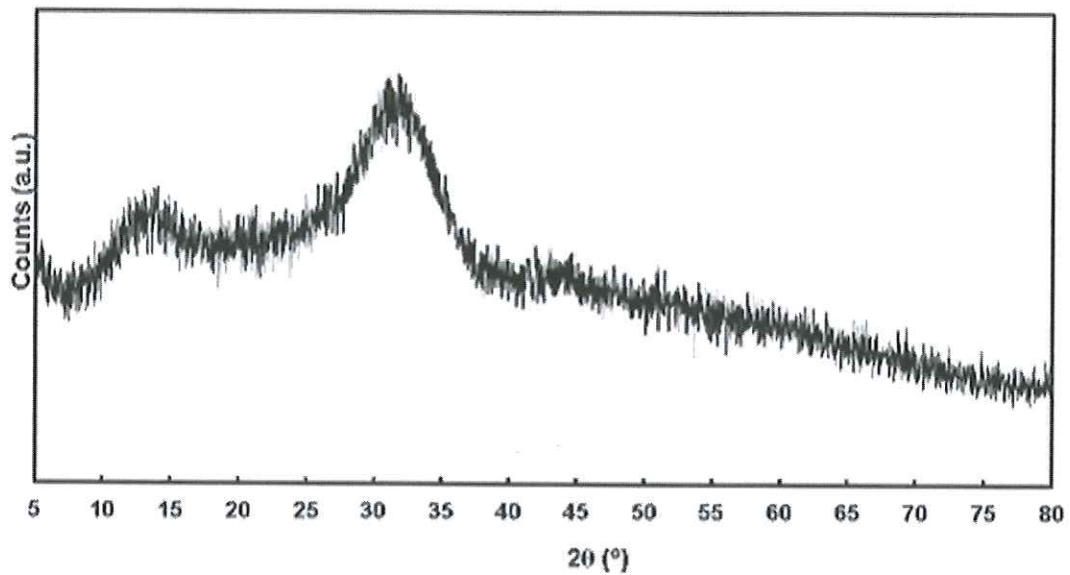

Figure 40: XRD results of the surface of bioactive glass at 0.2M nitric acid, sprayed at 70 mm with an enthalpy of 15 Ar- 25H2

Conclusions

The bioactive glass is a material with very important bioactivity, which is interesting in the medical fields. Indeed, it can bond with the body tissues and allows the bone to grow above it easily. Making bioactive glass coatings with plasma spraying on titanium substrate, is the ideal compromise to obtain the best bioactivity and mechanical properties. The sprayed material was either made with casting and crushing or in sol-gel but always sprayed as a powder or a suspension. This study has been started to try in spraying the sol-gel material as a solution, because it should have better microstructure and properties. This technique is very new and very few studies have been done about it.

The characterisation of the material allows to know that the solution with the catalyst react better as shown with its viscosity and gelation time. Also, the XRD of the powder and coatings allows to assert that the synthetized bioactive glass is actually amorphous, which qualify this technique to making bioactive glass.

The obtained bioactive glass solutions have a composition (table 11) very similar to the 45S5 glass. The thermal characterisation has given results similar to the results that can be found in the literature about the Bioglass®. Moreover, the solutions and the coatings have shown a perfectly amorphous state (fig 33 and 39).

The various tests have demonstrated that the optimal conditions are for the solution 0.2M of catalyst and at least 24 hours of homogenization. Then for the plasma spraying conditions: a spray distance of 70 mm and an enthalpy of 15 slpm of Ar and 25 slpm of H_2.

All the coatings of solution without catalyst have given very poor adherence. This can be explained by the fact that at the moment of spraying, the viscosity of this solution was very few comparing with the 0.2M solution in the same conditions (fig 25 and 26). The lack of adherence is probably due to the non-advanced state of hydrolysis and condensation reactions. This leads to a non-homogeneity of the solution and while sprayed, the precursors were probably sprayed without reacting.

This hypothesis is also supported by the gelation time (fig 27). Indeed, the 0M gelation time is lesser than the gelation of the 0.2M solution. Even though, this property did not explain the differences between the two coating because the gap between the two gelation times is only 4 days.

It would be interesting to continue this work in the future by doing biological tests on the samples coated with these optimal parameters to characterise their bioactivity. Also, the parameter of roughness can be taken into account as a factor of influence of the adherence. The investigation can also be continued further by spraying this sol on a titanium samples, with the same parameter. The results are expected to be better with the titanium sample, since the bond coat is in titania, the adherence will be higher. Also, the parameter of roughness can be taken into account.

Acknowledgments

63

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