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in

"Surface Treatments for Industrial Applications"

Brazing of Alumina/304 Stainless Steel for rotating joint applications

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Abstract

Mechanical face seal is a type of seal widely used in rotating equipment. They apply in all instances where movement is required, from robotics to automotive. Among the many existing fields of application, pumping systems are quite demanding in terms of performance, especially when the device has to be used in harsh environments.

The aim of the project was the development of the process for alumina (Al_2O_3) and 304 stainless steel in one piece for the realization mechanical systems (mechanical face seals) working in chemically aggressive environments.

Vacuum brazing technique was selected as joining technique to overcome incompatibility in the nature of chemical bonds of the materials involved. Home-made copper-based active brazing alloy (ABA) prepared starting from powders and binder was used to join two materials. A custom oven heated by IR-lamp until 1000°C was used to perform the brazing process.

The objective of the work was to study the process parameters: time of brazing, ramps of heating and cooling, temperature of brazing, issues in the join of chemically and thermo-mechanically different materials, amount of ABA to be applied and types of the binder.

Particular attention was given to the binder, changing the ease of brazing paste application and paste stability during storage, which are important factors for the industrialization of the process.

The process developed was shown to provide good integrity of the samples produced.

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Chapter 1

Introduction

1.1 General background and scope of work.

Mechanical face seals are widely used in mechanical engineering. They apply in all instances where movement is required, from robotics to automotive. Among the many existing fields of application, pumping systems are quite demanding in terms of performance, especially when the device has to be used in harsh environments.

Although it is composed of a complex group of components, a mechanical seal carries out its actual sealing action between two surfaces that are in relative motion to each other. One of these rings rotates together with the shaft, whereas the other one remains stationary and is an integral part of the casing. The figure 1 shows the components of a general mechanical seal [1]:

	Description	Materials
1	Spring	Stainless steel
2	Ring	Stainless steel
3	Gasket	Rubber
4	Slip ring	Various
5	Counterface	Various
6	Gasket	Rubber

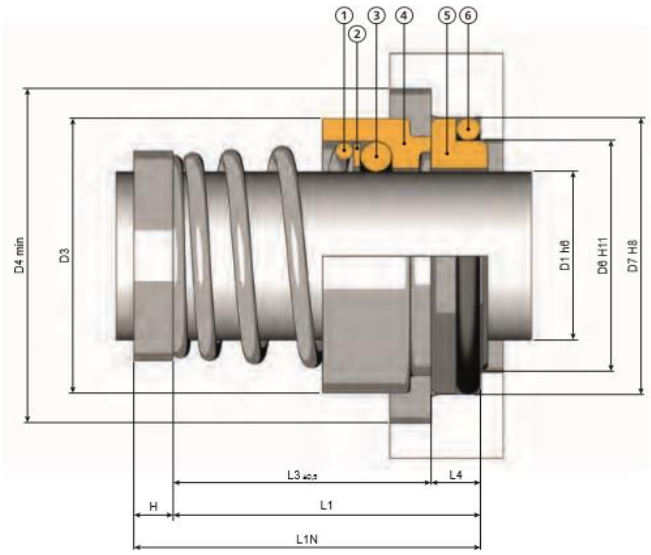

Figure 1:Mechanical seal drawing and materials used for parts

The mechanical seal shown is a single seal for standard duty composed by a fixed ring (4) and a rotating part (5) the can be made by various materials as stainless steel, alumina, PTFE and silicon carbide.

During rotation, the sealing surface of the rotating ring slides along the matching surface of the fixed ring. Thus, any leak must be present on this contact surface. Compressive force, which can be obtained either mechanically or hydraulically, is necessary in order to establish and maintain continuous contact between the rings. During operation, the seal must be able to withstand predetermined operating conditions without any loss, and one of these conditions is fluid pressure. This pressure can be used to increase the contact force with which the rotating ring presses against the fixed ring.

There are some factors that can affect the performance of a mechanical seal [2]:

- Friction
- Wear
- Adhesion
- Corrosive environment (outside joint)
- Surface stress
- Characteristics of the fluid

Friction and wear are the factors that have the greatest influence on seal characteristics and life. These phenomena are closely correlated and the combined effect leads to an alteration of the sliding surfaces, resulting in varying degrees of damage. Friction can be described as the resistance developed by material with respect to sliding contact. The value of the coefficient of sliding friction depends on the type of material comprising the sliding surfaces, as well as on the fluid itself. The sliding surfaces can undergo abrasive wear caused by the roughness of the contact surfaces. This phenomenon is defined as the scraping of one solid body by another.

Adhesion can be described as the transfer of a particle from one part of the contact surface to another and it can thus be defined as the interaction of two solid bodies in contact. This interaction takes place under certain conditions, generally with the contribution of heat.

When there is a corrosive atmosphere near the contact surface, adhesive wear and abrasive wear facilitate surface reactions. Surface oxidation can be beneficial when oxides are present and form a superficial protective layer on the sliding surface, whereas very hard oxides can act instead as an abrasive.

Sliding contact generates heat that facilitates and accelerates the elastic deformation of the surface until the fracture of the contact surface.

Pressure, composition, lubricating capacity of the fluid and duration of exposition are all factors of primary importance that can affect behavior in relation to wear on the sliding surfaces. Another important factor is the lubrication of the contact surfaces and the way in which this lubrication is carried out (full film lubrication, mixed lubrication, boundary lubrication or dry sliding).

The present project is focused on the development of the process for joining the ceramic and metallic elements in a particular for the realization of a mechanical seal which is a component of rotating element of devices working in either mechanically or chemically aggressive environments, such as those find in automotive applications and certain pumping systems.

Combining different materials is a known way of making seals achieving the desired objectives in terms of sealing, chemical inertness, reduced friction and resistance to wear. In particular, the introduction of alumina (or similar oxides) into a mechanical seal may provide the manufacturer with a convenient solution for the final application.

Our partner in this activity is a high-tech company, Meccanotecnica Umbra S.p.a., a world leader in the production of mechanical seals, specializing in the automotive and household appliance industries and in various industrial sector including chemical, pharmaceutical, food, pulp and paper, and mining.

This thesis is organized as follows: the present chapter introduces the general context and scope; Chapter 2 reviewes the basic theory of the joining and brazing processes; Chapter 3 describes the experimental set-up; Chapter 4 explains the details of the experimental procedure, while Chapter 5 is dedicated to the final considerations and conclusions.

1.2 Description of the experimental approach.

Joining of different materials is not an easy task. Brazing ceramics relies on wetting of the ceramic surface by some kind of metal, which is often hindered by the covalent nature of ceramic materials. To overcome this issue, there are two main brazing methods available to join a ceramic material to a metallic one:

- Indirect brazing, where the ceramic surfaces are metallized prior to brazing with conventional filler metals.

- Direct brazing, where the filler alloys contain active elements such as titanium, which are chemically reactive toward the ceramic materials.

Both methods are widely described in the technical literature [3]. In previous work of our group [4], were explored both methods and obtained satisfactory results with either indirect and direct techniques. Starting from his conclusion, we decided to adopt direct brazing method because of its greater intrinsic ease of application, which makes it potentially more suited to industrial upscaling.

Active filler brazing technique was selected for joining the alumina and steel elements of the mechanicals seals. Many realizations are possible of the technique, depending on factors such as the filler's composition and form (i.e., foil, wire, powder, etc.), the heating source (induction, resistance, electromagnetic radiation from different part of the spectrum) and the physical parameters of brazing (temperature, exposure time, cooling rate, etc.).

Powders form have been chosen because are more suitable for experimentation, changing the composition of elements it is possible to find a proper active brazing alloy (ABA) for the application required. In addition, the possibility to produce the selected ABA in house permits a remarkable reduction of process cost for our partner compared to the purchase of ABA's by specialized retailers. The ABA produced and used in the project is based on powders of copper (68% by mass), tin (23% by mass) and titanium (9% by mass). Two binders have been used to form the paste to be applied, one based on dextrin and the other based on xanthan gum.

In addition to that, the choice of heating source was made selecting an infrared ray lamp of 450W. For the heating phase was used a gradient of temperature of 5°C/min and during the cool-down step a ramp of 2.5°C/min.

Chapter 2

Brazing fundamentals

2.1 Metal to ceramic joining: Why?

Nowadays industry asks highly reliable products able to resist against extremely demanding conditions and in environments which require performances that no single material can show by itself. Thus the approach is selecting various materials providing, when assembled in the same structure, the required mechanical, thermal and chemical properties [5].

There are many applications in which both ceramics and metals can be employed to increase the performance and minimize the drawbacks. These include parts of engines, heat exchangers, cutting tools, articular prostheses, etc. [6].

The joining of dissimilar materials is becoming quite common and joining of ceramics with metals is a field where the research activity is intense. The comparison between metals and ceramics shows immediately that the latter usually have lower densities, are stiffer and harder but brittle, are poorer electrical and thermal conductors, are refractory and expand little when heated. Ceramics can also have very unique and wide ranging properties: for example, aluminum oxide is an electrical and thermal insulator, while aluminum nitride, despite being strongly electrically insulating, exhibits an high thermal conductivity. Metals tend to have different properties such as easier fabricability, electrical conductivity, low cost, but they generally do not possess the corrosion resistance and high durability of ceramics [7].

The practical use of assembled metallic and ceramic materials depends to a great extent on the ability to produce reliable joints; in other words, a metal-ceramic joint should have high mechanical strength, high durability and low production costs. To this end five major processes for bonding can be identified [8]:

- fusion welding, in which mating surface regions of components are molten and mixed before solidifying to form a permanent bond

- brazing, in which liquid metal flows into a narrow gap between the mating surfaces and solidifies to form a permanent bond
- diffusion bonding, in which mating surface regions of components are pressed together and heated to cause bonding and interdiffusion of the components
- glass sealing or glazing, which uses a fluid glass to bond mating surfaces in a process analogous to brazing or fusion welding
- adhesive bonding, in which component gaps are filled by fluid organic compounds which polymerize to form rigid bonding interlayers

Although there is a very large number of various processes which can be used in principle to make a joint, those which can be applied in practice, to satisfy a particular joining need, are often very limited in number. This restriction arises because there can be incompatibility between the fabrication or joint working conditions and the characteristics of the product or joining material.

2.2 Why brazing?

Usually conventional fusion welding is not performed on metal-ceramics assemblies due to the risk of brittle fracture initiation as a result of the high thermal stresses developed on cooling. On the other hand, adhesive bonding is not suitable for high service temperature applications and has a tendency to lose strength with long service. Hence, diffusion bonding and various types of brazing are currently applied to join ceramics to metals with the objective to maintain the excellent base-material properties of ceramics.

Brazing possesses a major advantage compared with conventional welding: the base materials do not melt. This allows brazing to be applied to join of dissimilar materials which cannot be joined by fusion processes due to metallurgical incompatibility, as it is the case of ceramics and metal.

In general brazing produces less thermally induced distortion since the entire component is subject to the same heat treatment, thus preventing the onset of localized thermal gradients which may cause distortion in welding. Finally, brazing is readily applicable to mass-production techniques, which is of paramount importance for the manufacturing engineer. In fact, it is relatively easy to automate, because the application of heat does not have to be localized and the application of filler metal is less critical, compared to fusion welding. In practice, given the proper clearance conditions and heat, a brazed joint tends to form by

capillary action and is not dependent on operator skill, contrary to most fusion welding processes [9].

2.3 Theoretical aspects

Brazing comprises a group of joining processes in which coalescence is produced by heating to suitable temperatures above 450 °C and by using a filler metal that must have a liquidus temperature above 450 °C and below the solidus temperature of the base metal. The filler metal is distributed between the closely fitted surfaces of the joint by capillary attraction. Brazing is distinguished from soldering in that the latter method employs a filler metal having a liquidus below 450 °C [10].

Brazing has four distinct characteristics:

- The coalescence, joining, or uniting of an assembly of two or more parts into one structure is achieved by heating the assembly or the region of the parts to be joined to a temperature of 450 °C or above.
- Assembled parts and filler metal are heated to a temperature high enough to melt the filler metal but not the parts.
- The molten filler metal spreads into the joint and must wet the base-metal surfaces.
- The parts are cooled to freeze the filler metal, which is held in the joint by capillary attraction and anchors the part together.

There are several physical principles and phenomena important for the brazing process: capillary motion, wetting, diffusion and metallurgical reactions.

Capillary motion

The capillary motion or capillarity is the ability of a liquid to flow in narrow spaces without any assistance. It is the dominant physical phenomenon that ensures a satisfactory brazing joint when both faying surfaces to be joined are wet by the molten filler metal. The capillarity acts due to the relative attraction of the molecules of liquid to each other (surface tension) and those of the solid (adhesive forces) thus influencing the brazing filler metal flow upon melting. The joint must be properly spaced to permit efficient capillary motion and coalescence. Actually, brazing filler metal flow is also affected by dynamic considerations involving viscosity, vapor pressure, gravity, and by the effect of any metallurgical reactions between the filler metal and the base material [11].

Wetting

Wetting can be defined as the ability of a liquid to maintain contact with a solid surface. It is the result of intermolecular interactions between solid and liquid. Wettability describes the degree of wetting of the solid by particular liquid rather than another. The phenomena of wetting and spreading are very important for the formation of a brazed joint [12]. High wettability guarantees that molten brazing filler metal is going to adhere to the surface of the material in the solid state and, when cooled below its solidus temperature, to make a strong bond with this material. The wetting is a function not only of the nature of the filler metal, but also of the interaction degree between materials to be joined. It is evident that in order to achieve a good degree of wetting on a specific surface, a molten metal must show a sufficient affinity to it, that is, it has to be capable of dissolving or alloying with some of the metals through which it flows. Another factor that affects the wetting is represented by the impurities on the surfaces to be wetted. Oxide layers inhibit wetting and spreading, as do grease dirt and other contaminants, that prevent a good contact between the brazing filler metal and the base materials.

Diffusion

Diffusion is the net movement of molecules or atoms from a region of high chemical potential to a region of low chemical potential. This phenomenon occurs when a system is not at the equilibrium. Base material and filler metal interact through diffusion, the atoms of the filler metal in liquid state diffuse into the base material forming diffusion-bonds. The rate of diffusion is proportional to the temperature. Diffusion of the filler metal at the surface of metal base should be minimized for the best joint quality and diffusion can be limited by minimizing the heat input at brazing temperature [13].

Metallurgical reactions

Several metallurgical phenomena influence the behaviour of brazed joints and, in some instances, necessitate special procedures for their control. These base metal effects include:

- alloying by the brazing filler;

- carbide precipitation;

- stress cracking;

- hydrogen, sulphur, and phosphorus embrittlement;

The extent of interaction varies greatly, depending on compositions of both the base metal and brazing filler metal and on the thermal cycle used. There is always some interaction, except in cases of mutual insolubility.

2.4 Elements of brazing

Reliability and cost must be considered when designing a braze joint. Joint strength, fatigue resistance, corrosion susceptibility, and high- temperature stability are additional concerns that determine the selection of joint design, braze filler materials, and processing parameters. A careful and intelligent evaluation of the following elements is required in order to produce satisfactory brazed joints [14]:

- Base metal characteristics
- Filler metal characteristics
- Surface preparation
- Joint design and clearance
- Temperature and time
- Rate and source of heating
- Protection by an atmosphere or flux

Base metal characteristics

The strength of the base metal has a profound effect on the strength of the brazed joint. At the same process conditions, high-strength base metals produce greater joint strengths than those made with softer base metals. When hardenable metals are brazed, joint strength becomes less predictable. This is because more complex metallurgical reactions between hardenable base metals and the brazing filler metals are involved. These reactions can cause changes in the base metal hardenability and result in lower than anticipated joint strengths. The coefficient of thermal expansion (CTE) is another important parameter because the mismatch in this property, as in the case of alumina and stainless steel, generates residual stress that can lead to distortions or cracks and in general affects the strength of the joint.

Filler metal characteristics

The second material involved in brazed structures is the filler metal. Brazing filler metals must possess four basic characteristics to yield quality joints. First, filler materials must have mechanical and physical properties to meet the intended service conditions. These include ductility, toughness, corrosion resistance, electrical and thermal conductivity, as well as temperature and fatigue resistance. The CTE of the filler metal should closely match that of the materials being joined or, where severe gradients exist, bridge the difference in CTEs. Second, the melting point of the filler metal should be below the solidus of the base material but as high as necessary to meet the operating temperature requirement. Third, the composition must be sufficiently stable that a separation of constituents or liquidation does not occur. Additionally, the filler metal must be chemically compatible with the mating materials to avoid adverse reactions or subsequent corrosion. Finally, the brazing filler metal must have the ability to wet the surfaces to be joined to form a continuous quality joint

Several filler alloys are available, depending on the materials to be joined, the joint design and the application of the workpiece. The table 1 [15] lists family of fillers for composition, available forms and applicability in accord with the American Welding Society (AWS):

Table 1: Summary of fillers: forms, materials joined and applications

Alloy family and type	AWS designation	Forms	Base materials joined	Major applications
Al-Si, eutectic	BAlSi	Preforms, wire, rods, foil, powder, RS foil(a)	Aluminum and aluminum alloys, steel to aluminum and aluminum to beryllium	Car radiators, heat exchangers, honeycomb aircraft structures, structural parts
Cu-X, solid solution Cu-Zn, peritectic Cu-Sn, peritectic	BCu RBCuZn None	Preforms, wire, rods, foil, powder, RS foil	Copper and copper alloys, copper to mild steel, copper to stainless steel	Heat exchangers, structural parts, automotive parts
Cu-P, eutectic	BCuP	Preforms, wire, rods, foil, powder, RS foil	Copper to copper, copper to silver oxide powdered metal composites	Electrical contacts, bus bars, heat exchangers
Cu-Ag, eutectic	BAg	Preforms, foil, powder	Most ferrous and nonferrous metals, except aluminum and magnesium	Most widely used utility filler metals
TM-Si-B(b), eutectic	. . .	. . .	. . .	. . .
(Ni/Fe + Cr)-Si-B	BNi	Powder, tape(c), RS foil	AISI 300 and 400 series steels and nickel- and cobalt-base superalloys, carbon steels, low-alloy steels, and copper	Aircraft turbine components, automotive parts, heat exchangers, honeycomb structures
(Ni,Pd)-Si-B	None	Powder, tape, RS foil	AISI 300 series stainless steels, cemented carbide, superalloys	Honeycomb structures, cemented carbide/polycrystalline diamond tools, orthodontics, catalytic converters
(Co,Cr)-Si-B	BCo	Powder, tape, RS foil	Cobalt-base heat-resistant corrosion-resistant superalloys	Aircraft engines, honeycomb marine structures
Au-Ni, solid solution	BAu	Preforms, wire, rods, foil, tape	Nickel-base heat-resistant alloys, steels	Honeycomb structures, structural turbine parts
Cu-(Ti,Zr)-Ni, eutectic and peritectic	None	Cladded strip, RS foil	Titanium/zirconium-base alloys	Titanium tubing, aircraft engines, honeycomb aircraft structures, aircraft structural parts, chemical reactors

The selection of the filler is a crucial part of the brazing, because an error in the choice can lead to a failure in the process. The figure 2 shows for any braze alloy family the temperature ranges in which can be used.

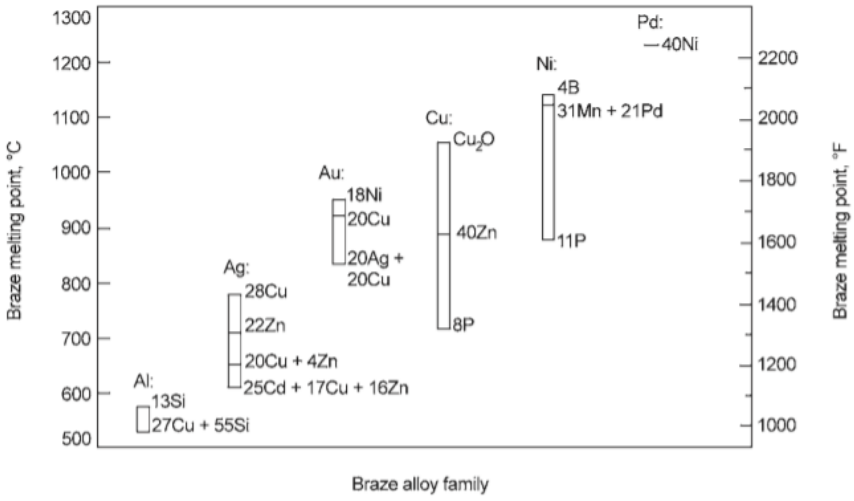

Figure 2: Brazing temperature ranges for various filler metals

With a brazing filler metal, joint strength is dependent on joint design, brazing temperature, amount of brazing filler metal applied, location and method of application, heating rate, and many other factors that constitute the brazing technique [16].

Joint design and clearance

There are, basically, two types of brazed joints and are showed in figure 3 [17]: butt and lap. The others joints are just a variation of them.

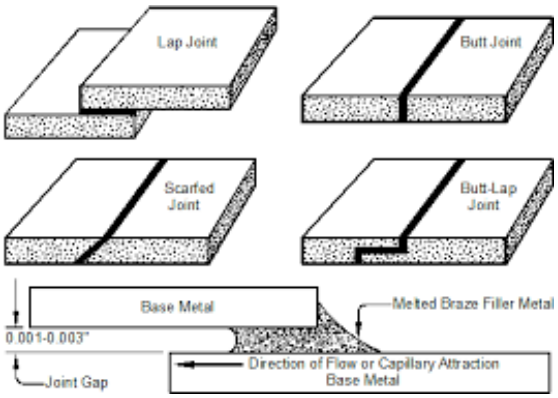

Figure 3: Common types of brazed joints

The butt joint configuration has some advantages, such as ease of preparation and a single thickness at the joint, which reduces stress concentrations. The drawback is that the thinnest member dictates the maximum strength of the joint.

The bonding area of a lap joint can be made larger than that of a butt joint. In fact, the area of overlap may be varied so that the joint is as strong as the weaker member, even when a lower-strength filler metal is used or when small defects are present in the final braze.

The butt-lap and the scarf configurations combine the advantage of a single thickness with maximum bonding area and strength but they require more complicated preparation and cannot be applied to thin pieces.

The clearance is the distance between the faying surfaces to be joined and affects the mechanical performance of the final piece [18]. It is strongly related with the amount of intermetallic phases present in the layers, the possibility of voids, the tensile strength of the final piece and the capillarity action which accounts for filler metal distribution. The relation between the tensile strength and the joint clearance is shown in the figure 4:

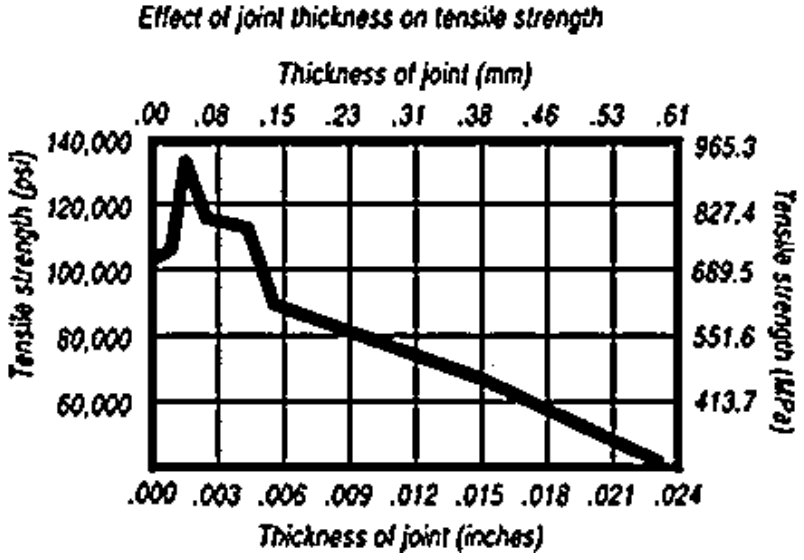

Figure 4: Tensile strength vs joint clearance

The smaller is the clearance, in situations where there is not extensive alloying and erosion, the easier it is for capillarity to distribute the filler metal throughout the joint area, and there

is less likelihood that voids or shrinkage cavities will form as the filler metal solidifies. Small clearances and correspondingly thin filler-metal films make stronger joints

In the design of a suitable joint is important to consider that an assembly expands during heating and that the joint gap may either widen or close by the time the filler metal starts to melt and move. Moreover, ensure that the filler metal amount is enough to absorb room temperature tensile stresses in order to compensate for any reduction in joint gap.

Surface preparation

The reproducibility of a brazing process depends strongly from the degree of cleanliness of the surfaces to be joined. This objective is not trivial to achieve, since contaminants tend to concentrate at surfaces.

In addition, it should be taken in account that metal surfaces consist of a thin oxide layer, formed by reactions with oxygen in the environment. The main effort in surface preparation is focused to removing those materials. Therefore, the brazing should be done as soon as possible after cleaning and etching.

There are two main groups of cleaning: chemical and mechanical [19].

Chemical cleaning is the most effective and include alkaline cleaning, solvent cleaning, vapor degreasing and acid pickling. The selection of the chemical cleaning agent depends on the nature of the contaminants, the base metal, the surface condition, and the joint design. Regardless the cleaning agent or the method used, it is important that all residue or surface film are removed from the cleaned parts by adequate rinsing to prevent the formation of other equally undesirable films on the faying surfaces.

Mechanical cleaning can be adequate, in cases that the design must permit it; the mechanical methods most used are dry and wet abrasive blast cleaning. The blasting technique is commonly used for surface preparation; the purpose of blasting is to remove all oxide film and to roughen the surfaces in order to increase the capillary attraction of the filler metal. The blasting material must be clean and must be of a type that does not leave on the surfaces to be joined any deposit.

Another technique in surface preparation is the use of solid and liquid fluxes; those compounds prevent, dissolve or facilitate removing of oxides and other undesirable surface substances.

Brazing methods

The brazing process can be led by several techniques [20]:

- Torch brazing: a torch is used to focus the flame at the joint assisted by a reducing flame to prevent the oxidation. The flame is generated by the combustion of a combination of oxygen and a fuel gas. With this process it is possible to use low-melting filler metals, which have excellent flow characteristics. Flux is normally required with the process to avoid the formation of oxides on the treated surface. This technique is widely used thanks the low cost of equipment. In the figure 5 two tubes of copper are brazed by torch brazing.

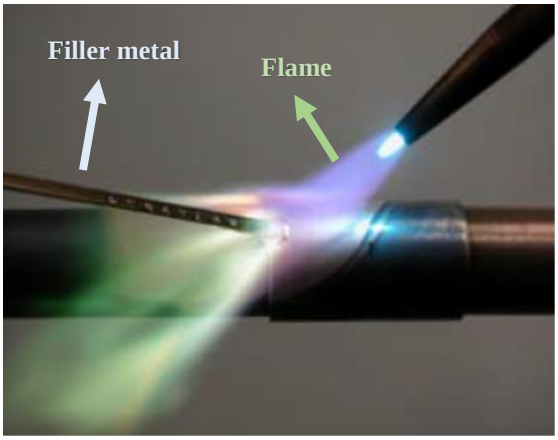

Figure 5: Torch brazing

- Induction brazing: the heat is generated from an electrically conductive element by electromagnetic induction through the eddy currents. The parts are pre-loaded with the filler metal and placed in a high frequency AC field. The frequencies ranging from 5 to 5000 kHz are used. Heating is localized to the part surface or just below, which is an advantage when joining components where metallurgical changes cannot be tolerated and on parts that allow minimal or no distortion. Most induction brazing occurs in air. Inductor design limits the complexity of assemblies, often making furnace brazing a more viable alternative for complex assemblies of several joints at one time. The process requires close, accurate part fit-up. Initial equipment cost can be high. The figure 6 shows an induction brazing of a component: how only

the part affected by electromagnetic field develops eddy current and resulting heating.

Figure 6: Induction brazing

- Resistance brazing: this process is very similar to spot welding. Both processes heat the base materials by sending direct current through the joint interface. While welding melts the base materials together, resistance brazing only melts the brazing filler metal. Resistance brazing process involves sending a direct current through the electrodes and the base materials. Resistance to this current by the electrodes, the base materials and their interface causes the base materials to heat to a temperature higher than the brazing alloy's liquidus. Once this is accomplished, a bond forms. In the figure 7 is possible to notice the heated piece during the resistance brazing process.

Figure 7: Resistive brazing

- Dip brazing: the heating of the joint is done by immersing of the workpiece in the molten salt or molten metal bath. In the first case, the filler metal is preloaded into the joint. In the case of molten metal bath, this contains the filler metal. The figure 8 shows an operator immerses a workpiece of aluminium in the molten salt bath.

Figure 8: Aluminium dip brazing

- Furnace brazing: the furnace is used for a medium to high volume of production and the heating is done by combustion, induction or resistive method. The charging of workpieces in a furnace brazing is showed in the figure 9.

Figure 9: Furnace brazing

- Infrared brazing: the heating is done by the invisible radiation from high-intensity quartz incandescent lamps. Lamps capable of delivering up to 5000 W of radiant

energy are commercially available. The lamps do not necessarily need to follow the contour of the part in order to heat it, but the heat input varies inversely as the square of the distance from the source. Compared with traditional joining methods, the rapid infrared joining technique has the following advantages: fast heating, little energy consumption, easy operation, no need for vacuum, little metallurgical modification to the base metal, and low cost.

Post brazing treatments and inspection

Joints brazed in a suitable atmosphere are bright and clean, therefore they require any further processing.

To relax the workpiece from the residual stress, thermal treatments after cooling are a well-known way in metal production and have already been successfully adopted in the case of joints between ceramic and metals with slight differences in CTE [21].

A quality control system should be adequate for both general and critical applications. Inspection of the assembly includes visual inspection, leak testing, radiographic examination and mechanical tests.

2.5 Ceramic to metal brazing

Achieving high integrity joints between ceramics and metals, as already mentioned, is a challenge. The properties of ceramics that make them attractive may pose major handicaps for joint fabrication. Due to the chemical inertness of ceramics and the different nature of chemical bonds, conventional joining methods for metals cannot be used. The success in joining a ceramic material to a metal by brazing depends at least on two main aspects: the thermodynamics and chemistry of the materials to be joined, that is to say the possibility and the way in which the materials are bonded, and the mismatch in the thermomechanical properties of the components, on which the level of residual stress and, along with it, the mechanical behaviour, depends.

The wettability of ceramics

Many important ceramic materials, such as alumina, are poorly wet by molten metals such as copper, silver or tin and exhibit contact angle values well above 90° [22]. Therefore, the main idea of indirect method is deposit a metallic film on the ceramic surface ready to braze using standard filler metals. Another more convenient way to achieve an important

reduction in the contact angle of a liquid metal on a ceramic substrate is by adding other metallic elements to the brazing alloy, typically group IVB elements, especially titanium.

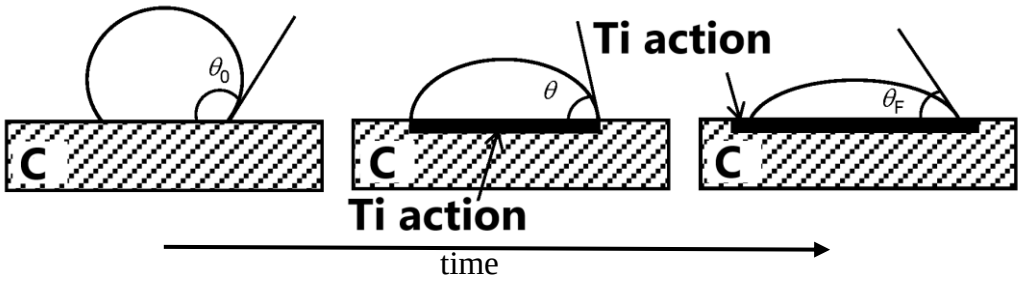

Figure 10: Ti action in the decreasing of contact angle between filler and ceramic surface

The addition of an active element induces a considerable improvement in the wettability, thanks to its chemical reactivity with the ceramic surface, which gives rise to a modification of metal-ceramic interface chemistry as showed in figure 10: the initial contact angle progressively decreases due to chemical reactions between titanium and aluminum oxide [23]. The chemical reactions and the microstructures at interfaces are very complex and, since they can relate to the bond strength and the reliability of the joint, they have been the subject of thorough investigations [24]. Kar's study [25] on characterization of interface of alumina (Al_2O_3) and 304 stainless steel (SS) braze joint using 97Ag28Cu3Ti active alloy shows the presence of TiO, Cu_3Ti_3O and FeTi phases at the Al_2O_3 interface and FeTi and $Fe_{35}Cr_{13}Ni_3Ti_7$ phases at the SS interface confirmed through X-ray diffraction (XRD) and transmission electron microscopy (TEM) studies. The presence of various intermetallic phases at the interface is responsible for change in the microhardness results.

Residual stress

In general, the metal component of the brazing has a larger CTE than the ceramic member involved in the process.

The figure 11 shows a chart created with CES®, software that provides comprehensive database of materials and process information. Basically, metals occupy the upper left part of the graph as they have higher thermal expansion coefficent and lower Young modulus respect of ceramic meterials, indeed these occupy the bottom right part of the chart. It is

possible to notice the Kovar material, a nickel-cobalt ferrous alloy with a coefficent of thermal expansion close to that of ceramic materials.

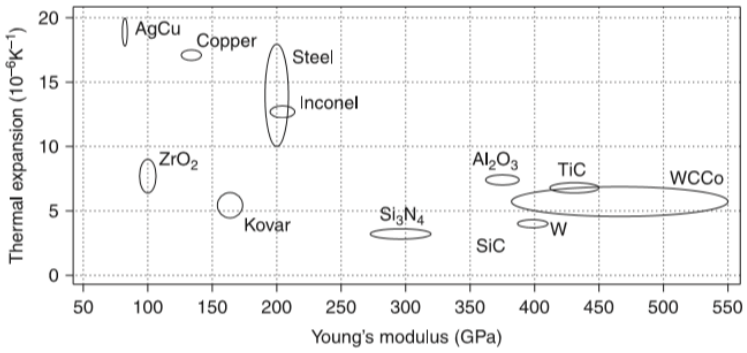

Figure 11: Young modulus vs CTE for different classes of materials

The result is the generation of residual stresses during the cooling of the assembly: at the interface the material with the lower coefficient of thermal expansion will be in compression (C) while the other in tension (T), as showed in the figure 12 [26]:

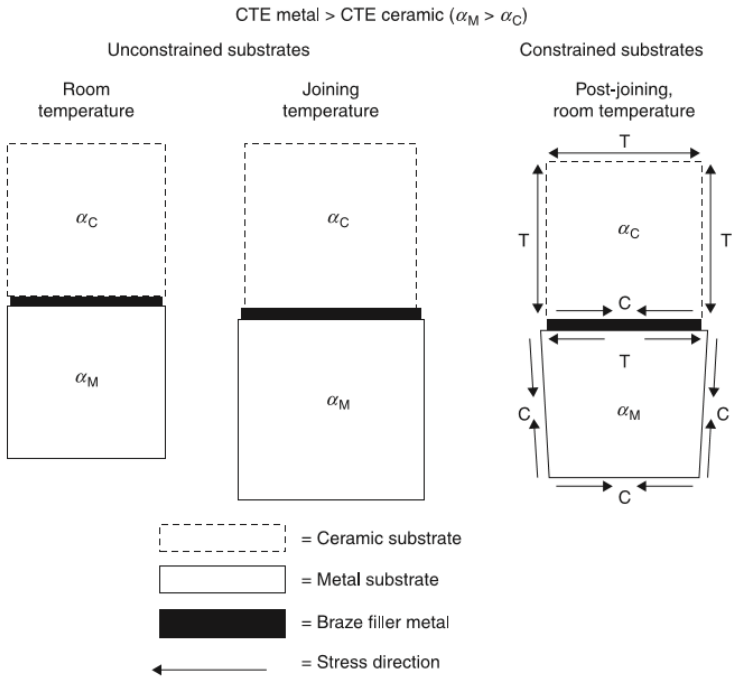

Figure 12: Residual stresses after joining due to difference in CTE's

The intensity and influence of these contraction stresses can be particularly marked for assemblies of ceramic and metallic components because of their very different thermal expansions and of the negligible ductility of ceramics. High integrity interfaces produced by selecting suitable materials and process parameters usually do not fail because of these residual stresses but their ability to resist external loads will be degraded [27]. Thus it is of vital importance to mitigate the effects of cooling stresses as much as possible. This is mainly a matter of a careful design aimed at minimizing the influence of the mismatch of thermal expansion coefficient.

There are two main approaches in the evaluation of the residual stresses, by finite element modelling and by experimental methods such as [28]:

- X-ray diffraction (XRD): it can provide reliable measurements of residual stresses on the external surface of the specimen (up to a depth of some microns) and, as a consequence, it is particularly suited for coatings.
- Neutron driffraction: neutrons can penetrate deep into most materials, therefore it is suited for residual stress analysis of bulk specimen.
- Micro-identation methods: it provides a rough evaluation of residual stress in the ceramic portion tested.
- Crack compliance methods: residual stresses are estimated by residual strain relaxation. The general procedure is to progressively cut through the specimen, measure released strain and use it to compute residual stresses via an analytical or numerical model. The most difficult problem in this method is the cutting of the ceramic which has to be performed without introducing additional stresses in the material. In case the ceramic is electrically conductive electro discharge machining (EDM) can be used.
- Layer peeling methods: this technique can be applied to beam- or plate-shaped specimens. A strain gauge is attached on one face of the sample to measure the strain induced by incremental grinding of the opposite face.
- Hole drilling methods: in several drilling processes a hole is machined. This material removal relieves residual stresses which can be estimated by measuring surface strains around the hole. The drilling procedure is particularly delicate: a low drilling depth per drilling step should be adopted and heat development has to be negligible.

Indirect brazing methods

There are several metallization methods [29], the most used for joining metal to ceramic are:

- molybdenum-manganese/nickel plating method: Also known as moly-manganese (Mo-Mn) metallization, a coating of molybdenum and manganese particles mixed with glass additives and volatile carriers is applied to the ceramic surface to be brazed, after air drying; the coating is heated in a wet hydrogen environment at 1450°–1600°C producing a "glassy" metallic coating 7–12 µm thick. A Nickel layer of 25-75 µm is after plated . The nickel plating is sinter-fired at 850°–950°C in a dry hydrogen atmosphere producing a metallized surface that can be readily brazed using standard braze filler metals.

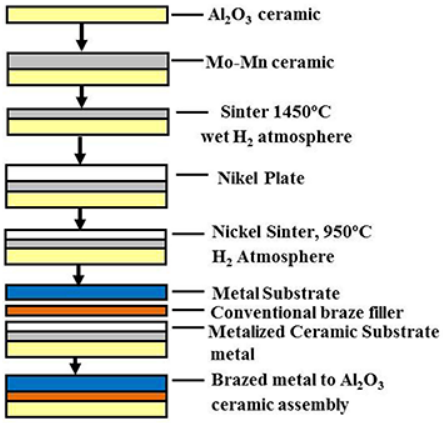

Figure 13: Scheme of Mo-Mn method

- Physical vapor deposition method: it is possible deposit one or more materials on the ceramic surface using a physical deposition method, such as evaporation or sputtering. The first layer deposited, usually 0.25-1 µm, is an element with high affinity for oxygen, as titanium, chromium, zirconium, niobium and hafnium, depending on the applications and service temperature of the workpiece. To prevent from oxidation the first layer, an intermediate layer or layers of noble metal (gold, platinum or palladium) are deposited. Now, the ceramic is ready to be brazed by using a standard braze filler metals.

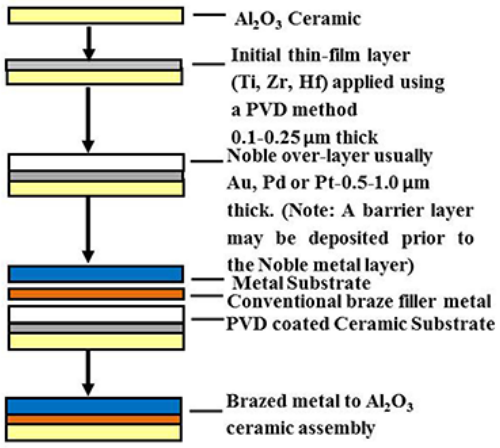

Figure 14: Scheme of PVD technique in the brazing process

Active filler-metal brazing

Active brazing has been developed to simplify the manufacturing of brazed ceramic joints: as already mentioned, the filler metal contains an active element (like Ti, Zr, ...) which promotes a good wetting of the ceramic surface and eliminates the need metallization treatments.

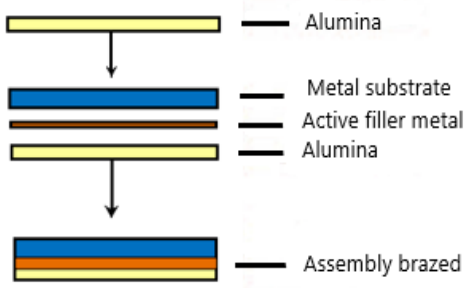

Figure 15: Scheme of active brazing

These elements are reactive respect of oxygen, therefore active brazing is conducted in vacuum furnaces ($\leq 10^{-5}$mbar). The filler alloy is usually Ag and Cu based, mainly for mechanical reason, and based on low melting elements such as In or Sn.

Chapter 3

Experimental set-up

This chapter describes the systems used to produce the components by brazing process and to characterize the samples by scanning electron microscopy (SEM) and by energy-dispersive X-rays spectroscopy (EDS).

Since the present of oxide in the faying surfaces to be joined is detrimental to brazing process and consequently to brazed piece quality, an oxygen-free environment is preferential for successful brazing. The active metals in the filler act like as “oxygen-getter” and an “oxygen-free” environment could be advantageous to improve the wettability of the ceramics.

There are two common ways to obtain the “oxygen-free” environment; use fluxes or a vacuum chamber. Fluxes prevent the formation of oxide on the faying surfaces to be joined but if the piece is exposed to high temperatures for a long time the flux could be evaporated and the process could be compromise.

The purity levels of atmosphere achieved in vacuum chamber are much higher than these obtained using fluxes. Also oxide layers on brazing parts are decomposed in a vacuum at high temperature, which improves base metal wetting resulting, in better joints properties as strength, minimum porosity, etc. [30].

A controllable oxygen-free environment helps to avoid the formation of oxide on the surface. This means that the probability of “oxygen-getter” in the active filler reacts with the oxygen on the ceramics and not with oxygen in environment is increased and consequently contribute to improve the joints properties. Therefore, the vacuum furnace was selected as brazing technique.

3.1 Vacuum system

A multi-purpose vacuum system was used to perform the furnace brazing process, showed in the figure 16:

Figure 16:The multi purposes vacuum system

It consists of four vacuum chambers connected to a central manifold via pneumatic gates. Starting from the drain, the system consists of a Varian dry Scroll pump with a flow rate of 210 $\frac{l}{min}$ that reaches a maximum vacuum of 10^{-2} mbar.

We find then a 3-way cross with two valves, an electro-pneumatic valve Pfeiffer and a manual angle valve VAT. The electro-pneumatic valve opens when the pump is switched on and closes with the its shutdown or in case of power failure. The manual valve, instead, allows the connection of the leak detector to the system to perform the leak detection without interrupting pumping in the chamber.

A turbo-molecular Pfeiffer follows with a flow rate of 360 $\frac{l}{min}$ to achieve a vacuum level up to 10^{-6} mbar. The turbo-molecular pump is connected to a central zone separated by the four chambers and the pump via five Varian gate CF63, each controlled by a different valve electro-pneumatic and operated by a LabVIEW programmed PLC, showed in the figure 17.

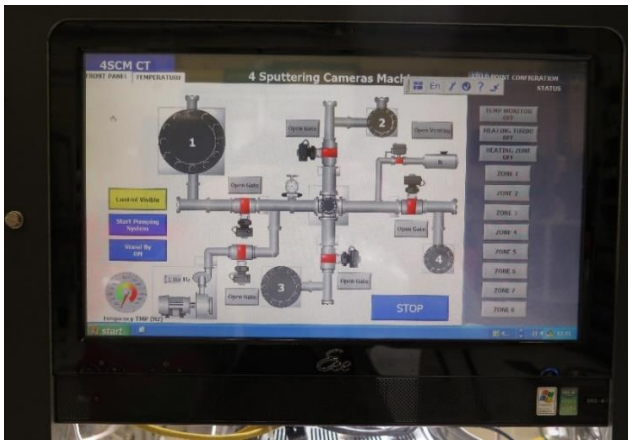

Figure 17:PLC control system

Two gas supply lines arrive at the central cross manifold: the one of nitrogen for venting and that of pure argon for sputtering. Nitrogen from the central supply line, whose pressure is controlled through a pressure regulator, enters through an all-metal angle Varian valve, while 99.9% pure argon is stored in a 15*l* air cylinder from which is introduced in the system.

The connection between the cylinder and the line uses a VCR (cajon) system, followed by an AD valve all-metal angle Varian and an all-metal dosing control valve of the VAT.

Two vacuum guages are mounted on the central chamber:

- PBR 260 Full range BA-Pi Pfeiffer (10^{3} - 10^{-10} mbar)

  Over the whole measurement range, the gauge has a continuous characteristic curve and its measuring signal is output as logarithm of the pressure. It functions with a Bayard Alpert hot cathode ionization measurement system and a Pirani measurement system. In a defined overlapping pressure range, a mixed signal of the two measurement systems is output. Above that range, the Pirani gauge signal prevails, while, below that range, the hot cathode signal only is output. The Pirani measurement system switches the hot cathode measurement system on and off to prevent filament burn-out and excessive contamination.

- Capacitance CCR 374 Pfeiffer (10^{3} - 10^{-4} mbar)

  The gauge consists in two chambers separated by a diaphragm, one connected to the vacuum system and the other to the external environment or to a reference system

with a known pressure. In front of the diaphragm there are two fixed electrodes, together they form a capacitor. When the pressure in the chamber changes, the diaphragm deflects and a capacitance variation causes an electrical signal proportionate to the pressure difference.

The chamber used in the brazing process is the number three, showed in the figure 18. Inside, there is the oven where the samples to be placed.

Figure 18:Chamber used as brazing furnace

3.2 The oven

The principle underlying the brazing furnace is basically blackbody radiation to exploit as much as physically possible the action of infrared radiation.

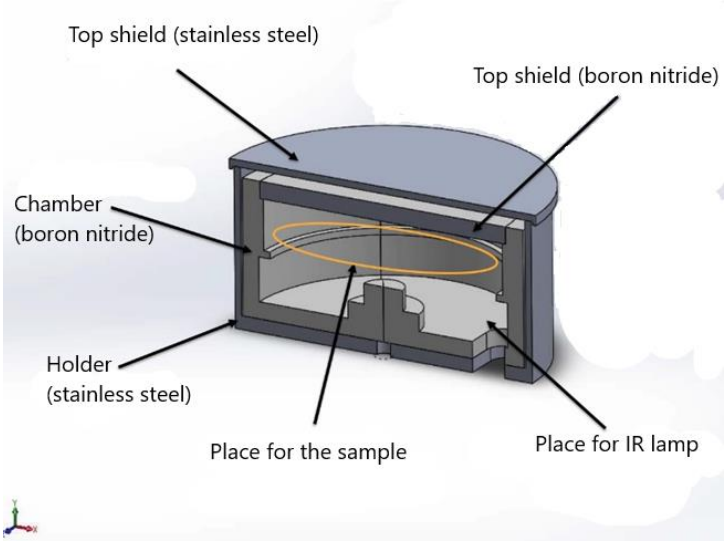

Figure 19:Section of the oven with the main elements

The oven has been designed to promote the melting temperature of the filler. The most important aspect was to make the appropriate thermal insulation in order to provide successful heating up to required temperature. As shown in the figure 19, a double insulation of ceramics and stainless steel was chosen. Sintered boron nitride was used to realize the ceramic part of insulation thanks to its high machinability in respect to commonly used alumina. The internal space of the furnace has 76mm of diameter and 10mm of length. As heating source, an infrared quartz lamp (IR lamp) of 450W and 76 mm of diameter was placed in the oven, as shown in figure 20. A grid of stainless steel holds the sample during the brazing.

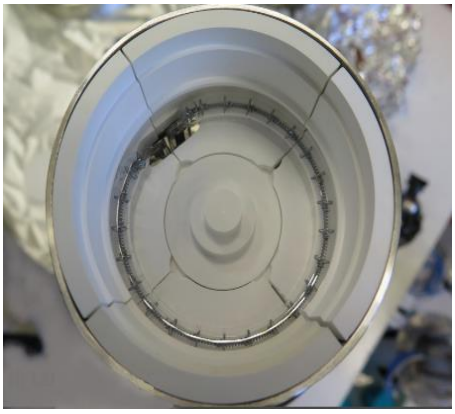

Figure 20: IR lamp used as heating source in the brazing process

The oven presents a kind of double box of boron nitride and stainless steel attached to DN100 CF flange and the temperature of the process was controlled by a K-type thermocouple connected to the grid, as shown in the figure 21.

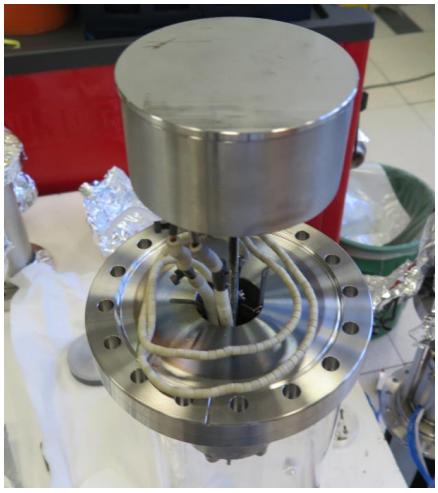

Figure 21:Oven, thermocouple and DN100 CF flange

In the figure 22, it is shown the oven mounted in the chamber.

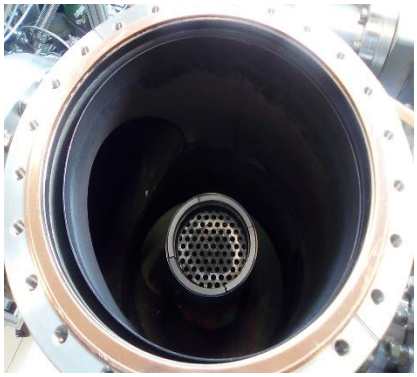

Figure 22: The oven is mounted in the chamber, the K-type thermocouple is connected to the grid

3.3 Heating control system

The IR lamp is equipped with a power supply device which is controlled by a GEFRAN 1600 module, where both final temperature and heating ramp are input. The controller adjusts the power supplied to the lamp according to the temperature sensed by the thermocouple.

Figure 23: Infrared lamp baking control and GEFRAN 1600

Gefran 1600 allows to set easily which temperature the system has to achieve and to set the gradient of temperature, in terms of degrees centigrade per minute (°C/min).

This is an important feature because permits to set different steps of temperature and different gradient of heating, as explained in the section 4.5 .

3.4 Characterization methods and testing

FEI (ex Philips) Scanning Electron Microscope (SEM) XL-30 (see figure 24) has been used to study the cross-section of the sample MTU1 with emphasis on the interlayer area, searching for evidence of filler metal diffusion into the base materials and integrity of the joint.

Figure 24: FEI SEM XL-30 used to study the sample MTU1

To study the sample, the brazed assembly was cut by a combination of Electrical Discharge Machining (EDM) and a precision diamond wire saw machine. The EDM technique was used in order to cut the metallic component and the diamond saw was used to cut the ceramic.

The SEM technique is one the most used instruments for microstructural characterization of solid object with high resolution (down to nm scale). A scanning electron microscope scans a focused electron beam over a surface to create an image. The electrons in the beam interact with the sample, producing various signals that can be used to obtain information about the surface topography and composition. The main SEM components include (see figure 25):

- source of electrons
- column down which electrons travel with electromagnetic lenses
- electron detector
- sample chamber
- computer and display to view the images

Electrons are produced at the top of the column by a gun (usually a tungsten filament), accelerated towards the anode by 5-30 KV potential and passed through a combination of lenses and apertures to produce a focused beam of electrons which hits the surface of the sample. The sample is mounted on a stage in the chamber area.

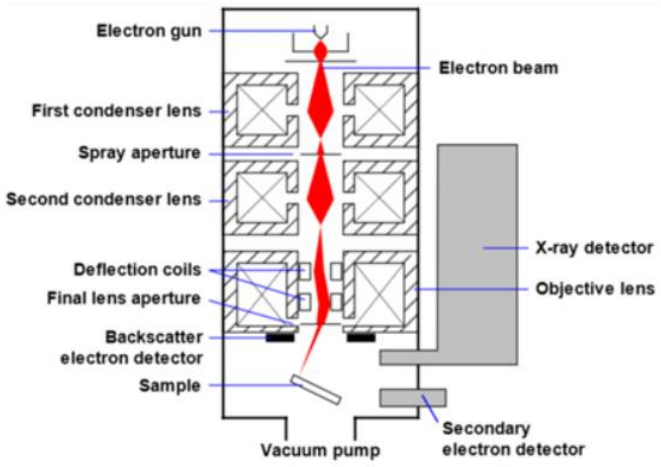

Figure 25: Scheme of the main parts of a SEM

The position of the electron beam on the sample is controlled by scan coils situated above the objective lens. These coils allow the beam to be scanned over the surface of the sample. This beam scanning enables information about a defined area on the sample to be collected. As a result of the electron-sample interaction, a number of signals are produced. These signals are then detected by appropriate detectors and used to produce an image on the monitor. The SEM imaging is carried out under vacuum since electrons cannot travel through the air for the necessary distance.

The interactions between high energy electrons and specimen produce several signals, shown in the figure 26.

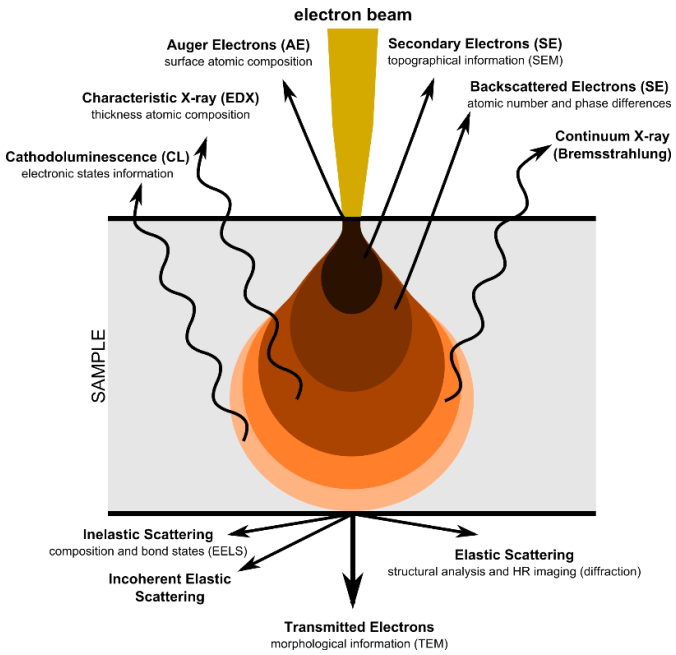

Figure 26:Volume of interactions after electron/sample collision

In the SEM analysis, mainly three signals providing different information about the sample:

- secondary electrons: since electrons in the conduction or valence band need a small amount of energy (work function) only to be transferred into vacuum, the energy of secondary electrons (SE) is low (>50 eV). Because of their low energy, SEs can only escape from the sample if they are generated close to the surface. Therefore, SE images are a means to get topographic images.
- Back-scattered electrons: the collision of an electron from the beam with a nucleus leads to the deflection of its path as a result of Coulomb forces. Sometimes, the electrons are completely scattered back and leave the surface of the sample. Since heavy atoms with a high atomic number are much stronger scatterers of electrons than light ones, they cause a higher signal. Therefore, images with back-scattered electron contain compositional information.
- X-rays: energy dispersive X-rays spectrometers is installed to have informations about the elemental composition of the sample.

The energy dispersive X-rays spectromers used for the analysis is the Brucker Quantax. EDS is a chemical microanalysis technique used in conjunction with SEM. The EDS technique detects x-rays emitted from the sample during bombardment by an electron beam

to characterize the elemental composition of the analyzed volume. Features or phases as small as 1 μm or less can be analyzed.

When the sample is bombarded by the SEM's electron beam, electrons are ejected from the atoms comprising the sample's surface. The resulting electron vacancies are filled by electrons from a higher state, and an X-ray is emitted to balance the energy difference between the two electrons' states. The X-ray energy is characteristic of the element from which it was emitted, therefore is possible measuring the elemental composition of the sample.

Chapter 4

Experimental procedure

This chapter describes which materials are used in the brazing process and how they are assembled for the brazing process.

4.1 Materials

Making a ceramic-metal joint is a process which involves at least three materials: the ceramic, the metal and the brazing filler. The MTU company has provided materials of interest for its purpose, while INFN – LNL researchers had the task of identifying a reliable brazing filler, as well as which method to use and design the process and the oven.

Base materials

MTU company supplied the following base materials, whose features are reviewed:

- Stainless steel 304: Austenitic Cr-Ni stainless steel, possessing high ductility, excellent drawing, forming, and spinning properties. Essentially non-magnetic, becomes slightly magnetic when cold worked. Excellent in a wide range of atmospheric environments and many corrosive media. Subject to pitting and crevice corrosion in warm chloride environments, and to stress corrosion cracking above about 60°C. Considered resistant to potable water with up to about 200mg/L chlorides at ambient temperatures, reducing to about 150mg/L at 60°C. The following table summarizes the typical elemental composition.

Table 2: Common composition of AISI 304 stainless steel

C	Mn	Si	P	S	Cr	Ni	N
0.08	2.0	0.75	0.045	0.030	18	8	0.10

- Alumina (Al_2O_3): also referred to aluminum oxide, is one of the most commonly used ceramic materials. The most common use of alumina is production of abrasives used to grind, clean, or polish materials and structural ceramics, but it is also used for refractories, pigments, catalyst carriers and in a variety of chemicals' formulations. The reason for its wide acceptance as a structural ceramic are its high hardness, excellent wear and corrosion resistance, and low electrical conductivity. It is also fairly cheap to manufacture, involving low-cost alumina powders that can be consolidated by variety of the methods (press and sinter, isostatic pressing, extrusion, etc.). For what the present work is concerned, the alumina elements provide sealing in the rotating joint piece.

The samples have a ring shape, described in the figure 27 and 28:

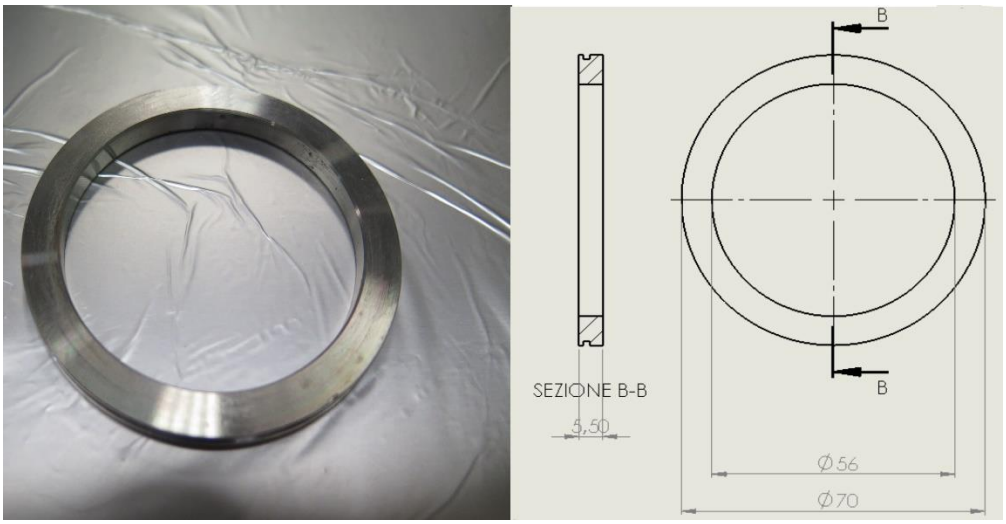

Figure 27: AISI 304 sample (left) and technical drawing (right)

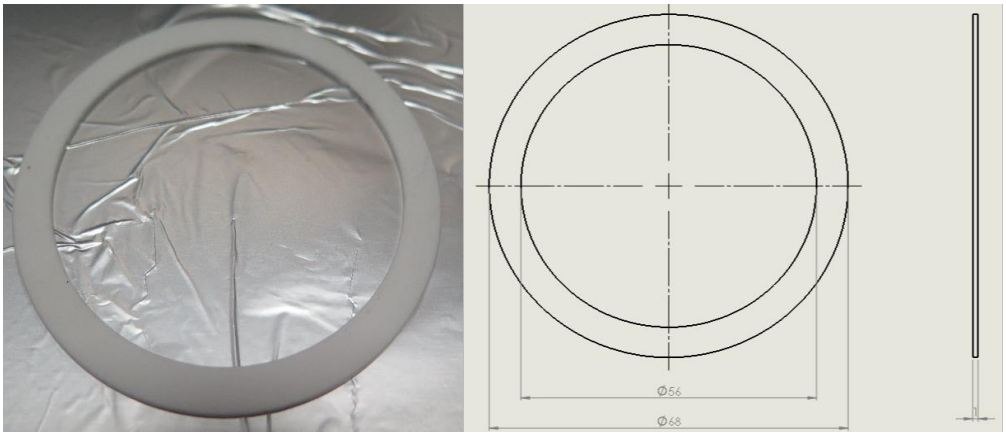

Figure 28: Alumina sample (left) and technical drawing (right)

It is possible to note that there is a difference of 2 mm between the outer diameter of the alumina ring and the corresponding dimension of the steel element. This difference makes

alignment of the two pieces a not-trivial process. An alignment device had to be designed and realized to overcome this difficulty; otherwise, the result can compromise the entire process and the use of the specimen as well.

An intrinsic difficulty exists when assembling such diverse materials like alumina and metal with respect to exposure to high temperature and, what is most important, subsequent cooling. In fact, the difference in the thermal expansion coefficients and Young's module of alumina and steel may induce residual stresses, especially in alumina rings, ultimately causing deformation and cracks.

For comparison purposes, the table 3 is provided below. It shows the coefficient of thermal expansion (CTE) and the Young's module of each materials involved in the brazing experiments taken from CES® software.

Table 3: Physical properties of materials at 20° and 800°C

Material	**CTE (µm/m °C)**		**Young's module (GPa)**	
	20°C	**800°C**	**20°C**	**800°C**
AISI 304 stainless steel	15	18.7	200	128
Alumina	7	8.5	366	366

Active brazing alloy

Several commercial brazing fillers are available, in terms of formulations and forms (wire, foil, paste, powder). An intense research work was carried out at the INFN – LNL in order to find the most economical, simple and performing solution for MTU company. A major challenge is choosing a formula which fit for purpose of brazing alumina and steel, which cannot obviously be brazed with any brazing alloy. On the other hand, chemical composition determines both filler's behaviour on melting and bonding between metal and alumina. The use of powders allowed to experiment different types of active brazing alloy

(ABA) composition and at the end to obtain an important reduction of cost. In fact, the work done permitted to produce in house without any purchase from suppliers.

This formulation of powders has been chosen:

- Copper 68% weight in powder form
- Tin 23% weight in powder form
- Titanium 9% weight in powder form

The role of copper is to provide the mechanical properties of the joint and the addition of tin permits the formation of an intermetallic compound with lower melting point, important property in terms of process. Finally, the addition of titanium alters the surface chemistry of the ceramic by the formation of intermediate reaction layer and lowers the wetting angle of the molten braze on the ceramic.

Table 2: Characteristics of the powders used

Powder	**% weight**	**Mesh**	**Purity %**	**Producer**
Copper	68	200	99	Alfa Aesar
Tin	23	100	98.85	Alfa Aesar
Titanium	9	395	99	Aldrich

The effectiveness of the filler powder also depends on its uniformity. An effective homogenization step is required for best results. A mixing technique has been used for obtaining a high degree of powder uniformity. The powders have been tumbled for eight hours with the Turbula T2F shaker, showed in the figure 17, in order to obtain as much as possible a homogenous mixture of powders. In fact, with a low degree of powder uniformity it is possible to have for instance micro-zone with different content of titanium, that means different ability of wetting the ceramic surface, and micro-zone with higher or lower content of tin that leads respectively lower or higher melting point of the ABA.

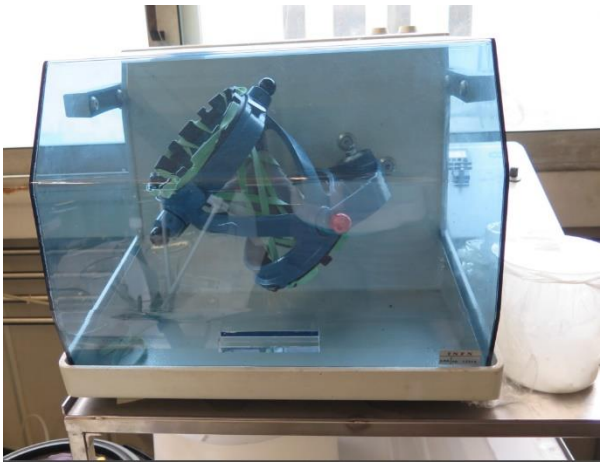

Figure 29: Turbula T2F shaker for powders

A polyethylene container was used for powders mixing and fastened in place by twisted rubber rings. The basket movement is driven by elastic drive belts by a drive gear. The frequency converter can vary the speed of the mixing. Tipically, a shaking frequency of one beat per second, continued for eight hours, provides acceptable results.

Binder

A powdered filler cannot be used as such in the brazing process, since no adhesion occurs upon contact of the powder with both metal and alumina. A binder is required to form a paste which achieves adhesion among the materials, under the conditions which will be described in the following.

The role of binder is crucial to obtain a paste easily and uniformly applicable on the sample and, in the future, during the industrial production. The binder must decompose at a temperature lower than the brazing temperature and it must form as less carbon residua as possible during the decomposition. In fact, the formation of carbon inclusions that affect in a hardly predictable way the mechanical behaviour of the joint.

To obtain these requirements, the following binders have been identified:

- Water and dextrin mixture, gives a paint consistence with a quick (minutes) drying time and it can be applied with a brush
- Water and xanthan gum mixture, gives a gel consistence with a longer (days) drying time. The xanthan gum is a high-molecular weight polysaccharide produced by the microorganism *Xanthomonas campestris* using microbial fermentation and is

primarily used as a thickener, but is also the most efficient stabilizer for suspensions, emulsions, foams and solid particles in water-based formulations. For its rheological properties, it can be applied with a syringe.

4.2 Surface preparation

A clean surface is imperative to ensure uniform quality and sound brazed joints. All grease, oil, wax, dirt, and nearly all oxides have to be carefully removed from the base and filler metals before brazing otherwise the capillary action of the filler and the wettability of the surface can be compromised.

The materials conditions do not require any particularly aggressive cleaning methods; on the contrary, oxidizing or chemically reacting solutions have to be avoided. Therefore, the following procedure was used:

- Washing in ultrasonic bath (US bath) into soap solution (Rodaclean) for 40 min at room temperature for AISI 304 sample (see figure 31)
- Washing in ultrasonic bath into deionized water for 30 min at room temperature
- Rinsing in ethanol
- Drying with nitrogen gas

Figure 30: Preparation of water and rodaclean for SS sample (left) and washing in US bath (right)

Indeed, the cleaning procedure used for alumina sample:

- Washing in ultrasonic bath into ethanol for 40 minutes at room temperature

- Rising in ethanol
- Drying with nitrogen gas

Once the cleaning is performed, it is recommended to proceed to brazing as soon as possible.

4.3 Preparation of the active brazing alloy and assembling of the sample

Ceramic and metal elements assembling is a critical step in the preparation of the specimen for subsequent brazing runs. While the use of a paste is convenient for specimen assembly, its behaviour depends on binder's properties. A few details are described about the performance of the dextrin and xanthan based binders.

A dextrin-based binder dries out quickly and quite a relevant amount of paste is lost by adhesion on the walls of the vessel used for preparation. The resulting paste is applied with a paintbrush, due to its relatively high viscosity (though not measured, it can be estimated in the order of hundreds of mPas). The accuracy of the application is limited, resulting in not uniform paste film thickness (at the level of fraction of mm) and in poor control of the smearing. Excess paste may leave traces of melted powder on the specimen, which can be points of attack of pitting corrosion events. In spite of all these drawbacks, dextrin-based paste is effective enough to prepare mechanically stable specimen for brazing.

The procedure of preparation was the following:

- Weight of powders (average 2.500 g)
- Addition of water (average 0.150 g)
- Addition of glue based on dextrin (average 0.100 g)
- Mixing up to obtain a paint consistence
- Application of paste obtained on the sample (see figure 32)

Figure 31: Application of filler by brush

The braze paste based on dextrin applied on the samples are summarized in the table 4:

Table 4: Paste applied on any sample and composition

Sample	Powders (g)	Water (g)	Dextrin (g)	Paste applied (g)
MTU 1	2.540	0.140	0.110	0.560
MTU 2	2.496	0.152	0.098	0.804
MTU 3	2.602	0.146	0.106	0.860
MTU 4	2.546	0.166	0.102	0.842
MTU 5	2.502	0.140	0.122	0.866
MTU 6	2.484	0.142	0.112	0.802
MTU 7	2.504	0.144	0.108	0.798
MTU 8	2.556	0.150	0.110	0.777
MTU 9	2.605	0.148	0.112	0.796
MTU 10	2.488	0.162	0.098	0.823
MTU 11	2.667	0.155	0.115	0.840
MTU 12	2.503	0.142	0.116	0.805

Xanthan-based paste introduces a few significant improvements in the filler application procedure. First of all, the amount of xanthan required to produce a paste of the desired filler concentration and viscosity is much reduced with respect to dextrin (approximately an order of magnitude less). A reduced amount of organic components is desirable because less carbon residua will form upon burning. A xanthan-based paste is quite resistant to drying and possess moderate adhesion properties, so that it does not stick on vessels and tools. A convenient mean for application is a syringe, with the advantage of the accurate

measurement of the volume of filler which is placed on the specimen without any waste. It is possible to prepare a high viscosity filler which does not smear upon application; this makes possible avoiding any unwanted smear-off of the filler itself.

The procedure of preparation was the following:

- Weight of powders (0.800 g average)
- Addition of xanthan gum (0.020 g average)
- Addition of water (0.100 g average)
- Mixing up to obtain a good consistence and placing in the syringe
- Application on the sample

The preparation is showed in the following figures:

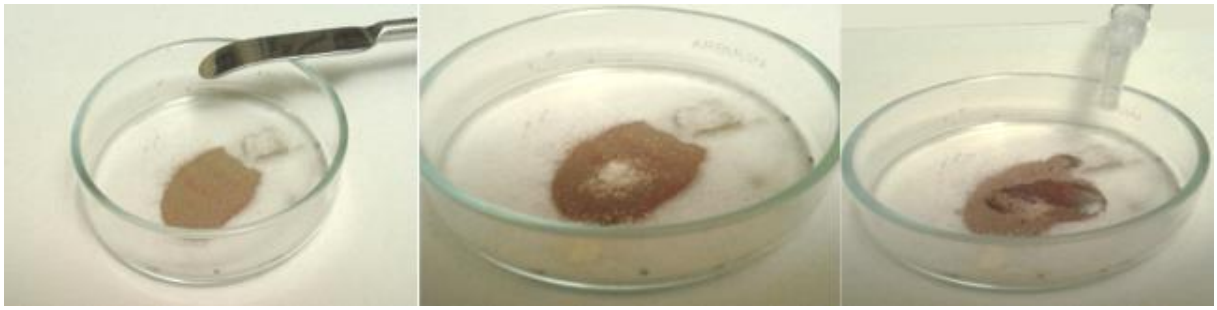

Figure 32: Starting from left CuSnTi powders; xanthan is added; finally, water is added

Figure 33: The filler is mixed and placed in the syringe

The braze paste based on xanthan applied on the samples are summarized in the table 5:

Table 5: Paste applied on any sample and composition

Sample	Powders (g)	Xanthan (g)	Water (g)	Paste applied (g)
MTU 13	0.801	0.020	0.110	0.870
MTU 14	0.798	0.022	0.102	0.855
MTU 15	0.806	0.019	0.098	0.860
MTU 16	0.803	0.020	0.102	0.868

Once the paste is applied, the sample is ready to be aligned and placed in the oven. The figure 35 shows a sample assembled:

Figure 34: Sample ready to be alligned and placed in the oven for the brazing process

4.4 Holder of alignment

During the brazing process, due to the melting of the filler and the spreading by capillary action, it is possible that the alignment of the two rings can be lost. The alignment is essential to obtain a sample that can be tested and can ensure the mechanical sealing. To avoid this issue, an holder of alignment has been design (see figure 36).

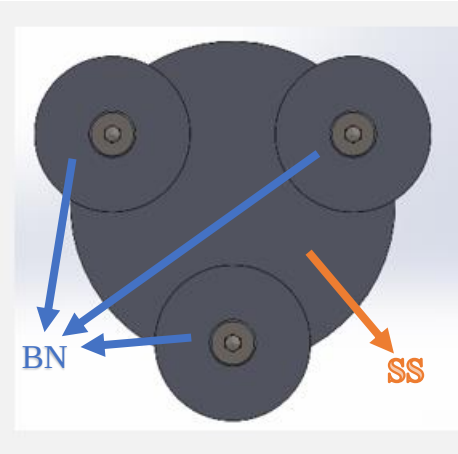

Figure 35: Drawing of holder of alignment

The holder consists in three cylinders of boron nitride (BN, 20 mm of diameter), screwed on a disk of stainless steel (SS) in order to have the three points of contact between the sample and the cylinders. Therefore, the disk has three holes on a circumference of 46 mm at 120° each other.

After the application of the ABA and the assembling of the sample, the holder was used to provide a first alignment waiting the drying of the ABA (some minutes). After that, the sample and the holder were placed on the grid inside the chamber, as shown in the figure 37.

Figure 36: The sample and the holder of alignment placed on the grid inside the vacumm furnace

4.5 Heating process

The brazing process chosen consists in seven temperature steps, showed in the chart 1:

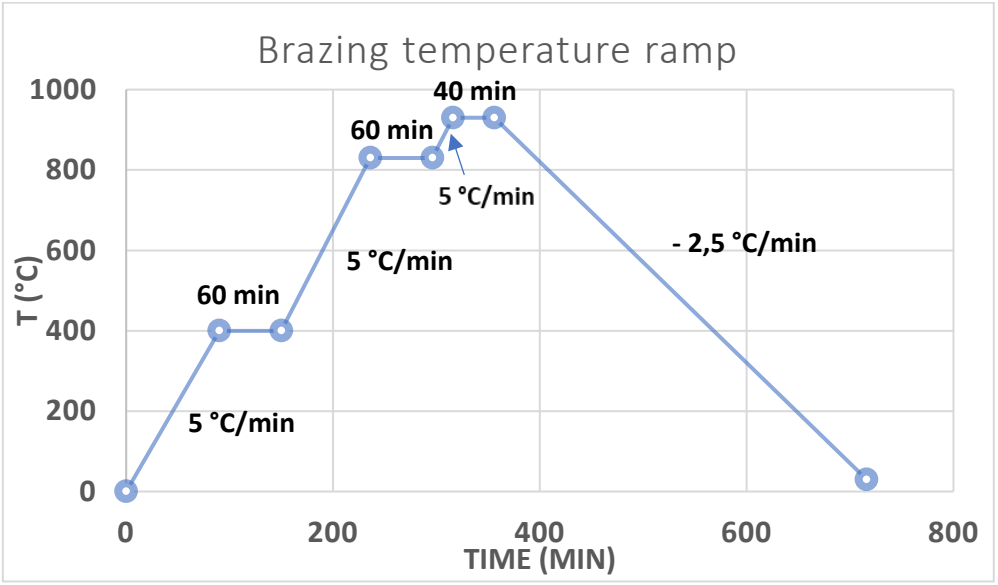

Chart 1: Brazing process for any samples

- From room temperature to 400°C by 5 °C/min ramp of heating (1h and 15 minutes).
- 400°C, 1 hour: the first temperature step is important to have the degradation of the binder and the aspiration of evaporated species from degassing in order to have a clean atmosphere in the chamber
- 400°C up to 830°C by 5 °C/min ramp of heating (1h and 25 minutes).
- 830°C, 1 hour: the second step provides an uniform temperature on the sample and ensures that the pressure is low enough (10^{-5} mbar) before to proceeding to brazing temperature
- 830°C up to 930°C by 5 °C/min ramp of heating (20 minutes).
- 930°C, 40 minutes: in the third step there is the melting of the filler, the spreading by capillary action and metallurgical reactions
- From 930°C to room temperature, by 2.5°C/min gradient of temperature.

The gradient of temperature in the step from brazing temperature to room temperature (2.5°C/min) was selected small enough to avoid the onset of residual stresses and possible consequent cracks on the alumina substrate due to the difference in CTE's.

The process has been the same for all samples in order to have a sound base of results for future developments. The table 2 shows the parameters of the process:

Table 6: Parameters of brazing process

Sample	**Base pressure (mbar)**	**Actual pressure (mbar)**	**Brazing T (°C)**	**Paste applied (g)**
MTU 1	$2.8x10^{-5}$	$4.6x10^{-4}$	901	0.560
MTU 2	$2.6x10^{-5}$	$4.2x10^{-4}$	915	0.804
MTU 3	$2.4x10^{-5}$	$4.0x10^{-4}$	913	0.860
MTU 4	$2.4x10^{-5}$	$4.8x10^{-4}$	913	0.842
MTU 5	$2.8x10^{-5}$	$4.2x10^{-4}$	910	0.866
MTU 6	$2.0x10^{-5}$	$4.2x10^{-4}$	925	0.802
MTU 7	$2.0x10^{-5}$	$4.8x10^{-4}$	923	0.798
MTU 8	$2.0x10^{-5}$	$2.2x10^{-4}$	923	0.777
MTU 9	$1.2x10^{-5}$	$3.2x10^{-4}$	922	0.796
MTU 10	$2.0x10^{-5}$	$3.4x10^{-4}$	920	0.823
MTU 11	$2.0x10^{-5}$	$1.2x10^{-4}$	922	0.840
MTU 12	$2.8x10^{-5}$	$4.8x10^{-4}$	923	0.805
MTU 13	$1.8x10^{-5}$	$3.2x10^{-4}$	921	0.870
MTU 14	$2.0x10^{-5}$	$5.2x10^{-4}$	923	0.855
MTU 15	$2.0x10^{-5}$	$4.2x10^{-4}$	925	0.860
MTU 16	$1.2x10^{-5}$	$2.8x10^{-4}$	908	0.868

The table 1 shows as the parameters of the brazing are similar for any samples, that means the process is reproducible.

The base pressure is the value of pressure achieved after one night of pumping while the actual pressure is the pressure during the brazing temperature (step 6 according to the graph1). The increment of pressure is due the heating (p and T directly proportional), the evaporation of water and the decomposition of xanthan, the vapour pressure of elements that form the ABA applied on the sample.

Differences on temperature are caused by the position of the thermocouple. In fact, the thermocouple is attached on the grid, so does not read the temperature of the ABA. It is possible that, during the placement of the sample on the grid, the thermocouple and the ceramic part of the sample are in contact. In a ceramic material, due to the low CTE, the temperature increases slower than a metallic one. This can explain why for the samples MTU1, MTU2, MTU3, MTU4, MTU5 and MTU16 the temperature read is lower respect of the other samples.

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Chapter 5

Experimental results

Sixteen different samples were processed according to the procedure described in previous chapter. In the following figures are shown the samples obtained by brazing:

Figure 37: MTU 1 (left) and MTU 2 (right)

MTU 1 is covered by a black layer, probably oxides the chamber was not very clean. It is not aligned and the ABA is present on the steel part, condition that can promote corrosion by pitting. Although the mentioned defects, the adherence seems good.

MTU 2 is cracked due to an error during the placement in the vacuum furnace: the sample was placed with the metallic part on the grid. In this configuration, as opposed to the placement with ceramic part on the grid, it does not exploit the gravity that helps to provide a good contact between the parts that is required to have capillary action. The consequence was a bad contact during the brazing and solidification that it has led not to complete adhesion.

Figure 38: MTU 3 (left) and MTU 4 (right)

MTU 3 is not aligned and the ABA is spread on the steel part, but the adherence seems good.

MTU 4 has a better quality in terms of apperance thanks a better application of the ABA paste.

Figure 39: MTU 5 (left) and MTU 6 (right)

MTU 5 is cracked, due to the breakdown of the heating system during the brazing process. The temperature has dropped drastically causing the cracking of the sample.

MTU 6 has a good apperance quality and the alignment is better than previous samples but not enough good for the aim. Starting from MTU 7, the holder of alignment has been introduced.

Figure 40: MTU 7 (left) and MTU 8 (right)

MTU 7 has a good alignment however a part of the ceramic ring was detached, as highlighted by light blue ellipse in figure 41, because it remained attached to the grid. The cause is probably the fall of ABA on the grid during the previous experiment. When the specimen has been removed, part of this remained joined to the grid.

MTU 8 has a good alignment and adherence however some traces of ABA are on the steel part.

Figure 41: MTU 9 (left) and MTU 10 /right)

MTU 9 is fractured due to another breakdown during the heating process. The brazing temperature was achieved but the rapid decrease in temperature has led to the cracking of the sample. The IR lamp was dismantled and reassembled to have a good contact and avoid possible failure of the process.

MTU 10 has good alignment and good quality, so it was sent to Meccanicotecnica Umbra.

Figure 42: MTU 11 (left) and MTU 12 (right)

MTU 11 and MTU 12 have good alignment and good appearance. They were sent to Meccanicotecnica Umbra.

Figure 43: MTU 13 (left) and MTU 14 (right)

The last four samples, (MTU 13, MTU 14, MTU 15 and MTU 16), were brazed with ABA based on Xanthan. The result in terms of alignment, quality and adherence is good for any samples. MTU 13 was cut to study by scanning electron microscopy (SEM), the others were sent to Meccanotecnica Umbra for further evaluations.

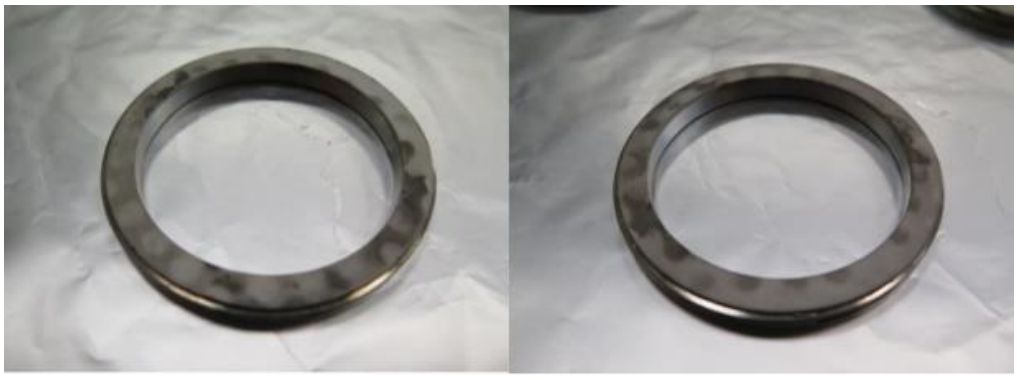

Figure 44: MTU 15 (left) and MTU 16 (right)

In the table 7 the results of the brazing process are summarized.

Table 7: Quality table.

Sample	**Paste applied (g)**	**Quality analysis**		
MTU 1	0.560	Not aligned	Good adherence	ABA spread on the steel
MTU 2	0.804	x	cracked	x
MTU 3	0.860	Not aligned	Good adherence	ABA spot spread on the steel
MTU 4	0.842	Not aligned	Good adherence	ABA spot spread on the steel
MTU 5	0.866	x	cracked	x
MTU 6	0.802	Not aligned	Good adherence	Good appearance
MTU 7	0.798	Aligned	Good adherence	Part of ceramic detached
MTU 8	0.777	Aligned	Good adherence	Few ABA spread on the steel
MTU 9	0.796	x	cracked	x
MTU 10	0.823	Aligned	Good adherence	Good appearance
MTU 11	0.840	Aligned	Good adherence	Good appearance
MTU 12	0.805	Aligned	Good adherence	Good appearance
MTU 13	0.870	Aligned	Good adherence	Good appearance
MTU 14	0.855	Aligned	Good adherence	Good appearance
MTU 15	0.860	Aligned	Good adherence	Good appearance
MTU 16	0.868	Aligned	Good adherence	Good appearance

Seven out of sixteen samples were sent to MTU for further evaluations, namely:

- Exposure to melted salt
- Pressure seal testing
- Test run on a rotating joint prototype

MTU 2 sample was cut to obtain a transversal section by electro discharge machining (EDM) technique and examined under SEM/EDS to magnify and analyse the circled area as in the figure below:

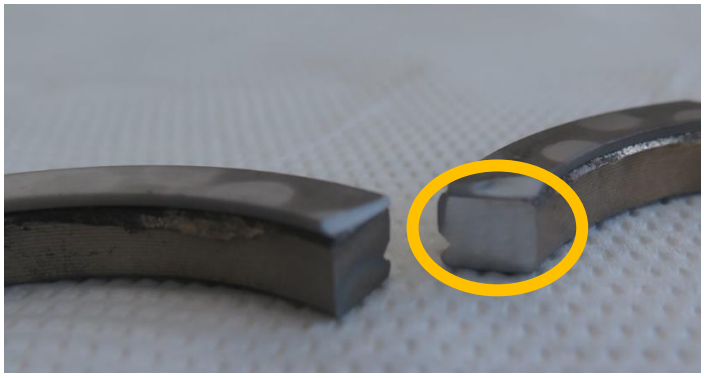

Figure 45: The sample was cut and lapped to obtain a transversal surface for SEM analysis

The following figure shows the result of EDS analyses:

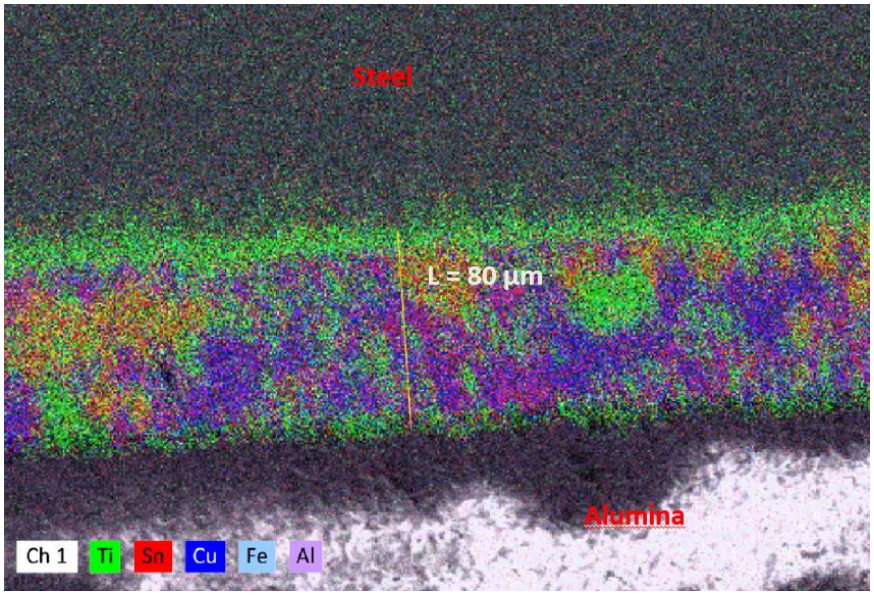

Figure 46: Mapping of elemental composition (MTU1)

The picture shows the details of the distribution of the elements across the joining layer, whose thickness is about 80 µm. The EDS analysis also evidences an almost symmetrical distribution of Ti at the interfaces between Fe and alumina surfaces; in particular, a layer of Ti is formed at the contact with alumina, thanks to its affinity to oxygen (which reflects in the close resemblance between Al_2O_3 and TiO_2). This layer is responsible of the adhesion of the filler to the alumina surface and the resulting mechanical integrity of the composite assembly. The other elements of the filler tend to populate the middle layer between steel and alumina, with the formation of intermetallic compounds which perform as binders. This situation is well described by the following graph of elemental distribution across the thickness of the joining area:

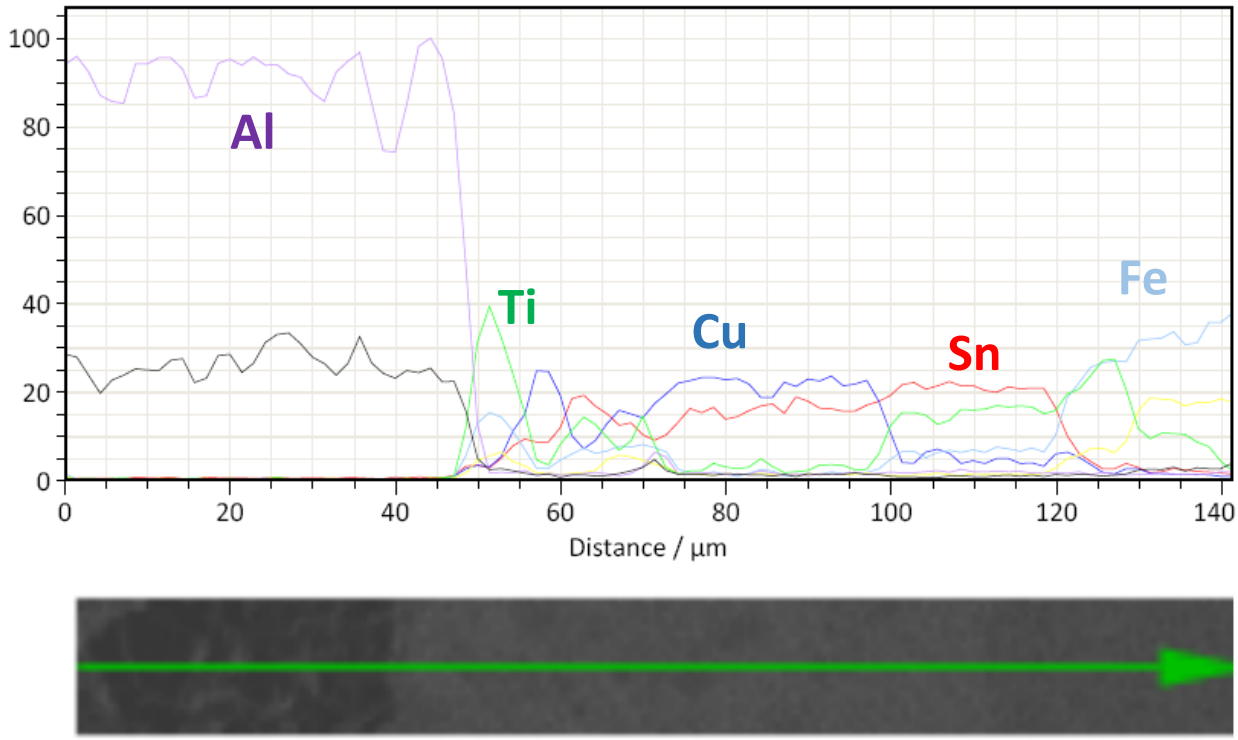

Figure 47: Elemental composition along a line of scan toward the brazed joint

It is worth to note the appreciable extent of diffusion of the filler's elements into the ferrous layer.

The sample MTU 13 was cut by EDM technique in the same way of MTU2. The result of SEM analysis is shown in figure

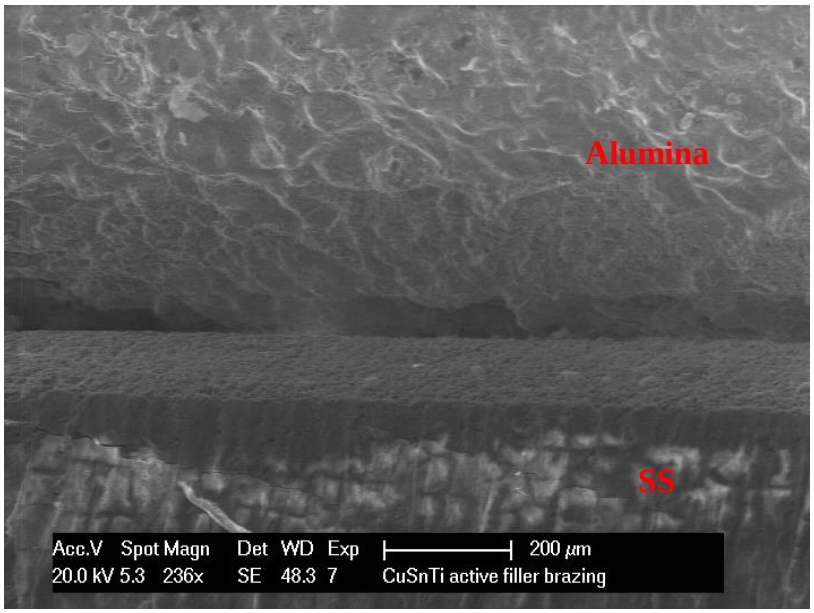

Figure 48: MTU 13 cross section under SEM

As it possible to see from the figure 49, the joint does not have any evident voids and defects. In first analysis, the use of xanthan as binder can replace the dextrin without evident drawbacks in terms of structural integrity of the joint.

Conclusions

The main conclusions of this work are summarized as follows:

- The vacuum brazing process developed for the preparation of mechanical composite components made of steel and alumina by means of ABA Cu68/Sn23/Ti9 at 930°C heated by 450W IR lamp proved to be valid and repeatable.
- A key step in the experimental procedure is the use of an innovative, xanthan-based binder for filler preparation. These resulted in an accurate application of the filler and in a reduced smear spreading over the specimens during brazing
- The procedure resulted in thirteen out of sixteen samples possessing good structural integrity of interface SS/Alumina.
- Six of them are presently under verification by Meccanotecnica Umbra s.p.a.

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