Universidade do Minho
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Reflow Soldering in an Oxidant Atmosphere

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Reflow Soldering in an Oxidant Atmosphere

Master Thesis
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Work done under the guidance of
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ABSTRACT

Reflow soldering process is the most used process in industry to solder the Printed Circuit Boards (PCBs). To ensure a good solder joint reliability, this process are normally made under an inert atmosphere like Nitrogen (N_2), in order to reduce soldering defects.

Since Nitrogen is an expensive element, it is intended to eliminate it from the process. This way, it is intended to the study of alternatives to reduce solder oxidation, in order to eliminate or reduce N_2 spending. These alternatives undergo by testing the soldering process in an atmosphere of Air, to evaluate the process window and consequences of soldering without Nitrogen. It is also study the influence of adding Nickel particles on the PCBs surface.

There was tested a real product (SolarA) at the Bosch Reflow production line, were used the standard process parameters, and made some tests at the University of Minho. The principal variables studied were the atmosphere, and the addition of Nickel particles on the PCBs/substrates before the soldering process. It was also studied the influence of temperature, and solders used, SAC405 and SAC305. From the inspection and characterization techniques were evaluate the presence of soldering defects, the solder joints geometry and constitution, intermetallic layer, solders melting temperatures, and the presence and morphology of the Nickel particles after soldering.

The results obtained reveal that it is possible to apply one Reflow soldering in an Air atmosphere, keeping the standard requirements, and being possible to accept the product. Soldering in an Air atmosphere, according to the automatic inspections, no errors were detected in the PCBs but only pseudo-errors that tripled. The wetting and spreading seems to reduce, and the intermetallic does not present large differences, being in accord with the Bosch requirements. The presence of Nickel particles at the Bosch tests seems to not have influence in the results. From the university tests, were verified that soldering in Air does not influence the melting temperatures of SAC405 and SAC305. With Ni particles addition it was possible soldering at 220°C, while without Ni it was only possible to solder at 240°C. The intermetallic thickness seems to increase with the temperature increasing. The Nickel particles are located inside the intermetallic layer, reacting with the Cu-Sn IMC and solder, decreasing intermetallic thickness, reducing the copper pad consumption.

KEYWORDS

Reflow - Soldering – Atmosphere – Air – Nickel

Resumo

O processo de soldadura Reflow é mais usado na indústria para soldar as Placas de circuito Impresso (PCI). Para garantir a fiabilidade da junta de solda, este processo é efetuado normalmente numa atmosfera de Azoto (N_2), para reduzir os defeitos de soldadura .

Sendo o Azoto um elemento caro, é pretendido eliminá-lo do processo. Desta forma, pretende-se estudar alternativas para reduzir a oxidação, a fim de eliminar os gastos de N_2. Estas alternativas passam por testar soldar numa atmosfera de ar, de forma a avaliar a janela de processo e as consequências de soldar sem Azoto. Também é estudado a influência de adicionar partículas de Níquel na superfície das PCIs.

Foi testado um produto real (SolarA) numa linha de produção da Bosch, utilizando os parâmetros de processo *standard*, e realizados teste na Universidade do Minho. As variáveis principais testadas foram a atmosfera, e a adição de partículas de Níquel nas PCIs/substratos, antes de soldar. Também foi estudada a influência da temperatura e das soldas usadas, SAC405 e SAC305. A partir das técnicas de inspeção e caracterização, foi avaliada a presença de defeitos, a geometria e constituição das juntas de soldadura, a camada intermetálica, as temperaturas de fusão, e a presença e morfologia das partículas de Níquel após a soldadura .

Os resultados obtidos revelaram ser possível soldar uma vez por Reflow numa atmosfera de ar, mantendo-se os requisitos exigidos, sendo possível a aceitação do produto. Soldar numa atmosfera de ar, através das técnicas de inspeção automáticas, nenhum erro foi detetado nas PCIs, mas apenas pseudoerros, que triplicaram. A molhabilidade e espalhamento parecem reduzir, e a intermetálica não apresente grandes diferenças, obedecendo aos requisitos Bosch. A presença de partículas de Níquel, nos testes da Bosch, parecem não influenciar os resultados. Através dos testes da universidade, verificou-se que soldar em ar, não influenciou as temperaturas de fusão da SAC405 e SAC305. Com adição de particulas Ni foi possível soldar a 220°C enquanto que sem Ni apenas foi possível soldar a 240°C. A espessura da intermetálica parece aumentar com o aumento da temperatura. As partículas de Níquel encontram-se localizadas dentro da camada intermetálica, reagindo com o composto intermetálico Cu-Sn e com a solda, reduzindo a espessura da camada intermetálica, reduzindo assim o consumo do *pad* de cobre.

Palavras-Chave

Reflow - Soldadura – Atmosfera – Ar – Níquel

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LIST OF ABBREVIATIONS

Ag	Silver
Ar	Argon
AOI	Automatic Optical Inspection
Cu	Copper
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
EDS	Energy Dispersive X-Ray Spectroscopy
ENIG	Electroless Nickel - Immersion Gold
FR-4	Flame Resistant 4
HASL	Hot Air Solder Levelling
IMC	Intermetallic compound
IPC	Institute for Printed Circuit
N_2	Nitrogen
Ni	Nickel
O_2	Oxygen
OSP	Organic Surface Preservative
Pb	Lead
PCB	Printed Circuit Board
PTFE	Polytetrafluoroethylene
QFP	Quad Flat Pack
RoHS	Restriction of Certain Hazardous Substances
SAC	Sn-Ag-Cu
SEM	Scanning Electron Microscopy
SMD	Surface Mount Device
SMT	Surface Mount Technology
SOT	Small Outline Transistor
Sn	Tin
SPI	Solder Paste Inspection
TGA	Thermogravimetric Analysis
TH	Through Hole
THT	Through Hole Technology
WEEE	Waste Electrical and Electronic Equipment

CHAPTER 1

INTRODUCTION

Electronical devices such Printed Circuit Board (PCB), have been a subject of a huge investment by the industry, due to its efficiency and applicability. It can be used in numerous applications like, microwave and washing machines that require simpler PCB, and products such as auto-radios and computers which require more complex devices.

Printed Circuit Board is the most common method to support and electrically connect electronic devices such resistances, capacitors, among other, creating the electronic circuits. For that is utilized a substrate (board) which is an electric insulating material, where are printed the conductor tracks and pads, that allow the electrical connection of the components to each other. These substrates can be formed by one or more Copper printed layers according to the complexity of the electric circuit, which is growing rapidly due to the high requirements of new electronic devices require [1].

With the development of more complex products, the PCBs requirements have increased due to the increasing of the packing density of the components. This results in: diminishing of the space dimension between the components; the holes diameters are decreasing; the conductor tracks are thinner; and the PCB boards have more layers. With this, the integrated circuits have become more complex (e.g. implementation of microvias), PCBs design has to be planned carefully and components assembly is more difficult [1].

The connection board-component is made from a soldering process creating a solder joint between them that is responsible for the mechanical and electrical connection. The soldering processes most used industrially are Reflow and Wave soldering. With these soldering processes it is possible to make mechanical and electrical connection between the components and the boards with a solder joint. The quality of the solder joints depends essentially of the type of solder, thermal cycle and the atmosphere used [2].

The solder joints need to be constantly studied with the development of PCBs, because the increase of components density and less space on the board results in a higher probability of defects to occurrence. This way, the thermal cycle must be planned so that the PCBs are subject to a specific temperature in a given period of time, in order to obtain an adequate intermetallic between the components, solder and pads [2].

Other parameter that influence the solder joint and the presence of soldering defects, is the atmosphere used. Normally the soldering processes use an inert atmosphere like Nitrogen (N_2), in order to reduce solder defects like oxidation, which may cause a bad solder joints. But the use of a high flow inert gas, normally involves high expenses [3].

This way, in partnership with Bosch Car Multimedia from Braga, was developed the project of "Reflow Soldering in an Oxidant Atmosphere". This dissertation is intended to: evaluate the influence of soldering in an oxidant atmosphere (Air atmosphere) on joint quality; evaluate the influence of soldering in an inert and oxidant atmosphere and with adding Nickel into the liquid flux. These studies are intended to evaluate the solder microstructure, intermetallic layer thicknesses and solder joints geometry, to quantify the defects, wetting and spreading.

1.1 Motivation

The soldering processes as Reflow soldering, allows to create an electrical and mechanical connection between the components and PCB boards, creating the solder joints. The characteristics of solder joints depend essentially of the type of solder, thermal cycle and the atmosphere used. These process parameters may influence the solderability of the solder, solder joints geometry, thickness of the intermetallic, wetting and spreading, this way, defects can appear.

To create these solder connections, the electronic industry traditionally used lead solders, namely the Sn-Pb (Sn63Pb37) solders, due to its high solderability and low melting point (183°C), comparably to other solders. But from 2006, the lead solders began to be forbidden due to their toxicity to the environment and human being according to European Union's Restriction of Hazardous Substances (RoHS) Directive and Waste Electrical and Electronic Equipment (WEEE) Directive. Then, to substitute the Lead solders, began to emerge the first lead-free solders (solders without Pb in their composition) in industry [4, 5].

The use of the Lead-free solders, according to their specification, soldering need higher temperatures (about 217°C) comparing to the temperatures used with Pb solders (about 183°C). This way, the increase of the soldering temperatures can cause problems such as higher susceptibility to oxidation and increasing of the energy expenditures. In other to avoid the oxidation problems, industries utilize a neutral atmosphere (e.g. N_2), but with this, the soldering processes costs increase, due to high cost of Nitrogen [3].

Since Nitrogen is an expensive element, it is intended, when possible, to eliminate it. This way, in partnership with Bosch Car Multimedia from Braga, was developed the project of "Reflow Soldering in an Oxidant Atmosphere". At this dissertation is intended to the study of alternatives to reduce solder oxidation, in order to eliminate or reduce N_2 spending. These alternatives undergo by testing the soldering process in an Air atmosphere, and the addition of an alloying element in the soldering process.

1.2 Objectives

This project has the main objective, the study of alternatives to reduce solder oxidation, in order to eliminate or reduce N_2 spending.

Specific Objectives:

- Evaluate the influence of soldering in an oxidant atmosphere (Air atmosphere) in the solder joints geometry, presence of possible soldering defects, and in the intermetallic thickness;
- Evaluate the influence of soldering in an inert and Air atmosphere, with adding Nickel micro particles into the liquid flux.

1.3 Dissertation Structure

This dissertation is divided into five chapters.

In chapter 1 is presented a brief overview of this thesis work where are presented the motivation and the objectives to be achieved.

In chapter 2 is approached the review of the literature with the concepts related to the project theme. First are presented the concepts related to the Printed Circuits Boards and components. Secondly are presented the concepts related to soldering, like the solders used, soldering processes and parameters, and finally are presented some of the soldering defects that exist.

In chapter 3 are presented the materials and experimental methods used in this project. It is presented: all the materials used in the project realized at Bosch Car Multimedia and at the University of Minho; the processing methods which are explained the procedures and parameters used at Reflow soldering process; the inspection and qualifying techniques used to qualify the products produced at the production; finally are presented the characterization techniques used.

In chapter 4 are presented and discussed all the results obtained from the characterization techniques. In this chapter as the previous, were divided the results obtained at Bosch and the results obtained at University. First are presented the results obtained in the inspection and qualifying techniques, then are presented the results obtained in the characterization techniques for each condition used (soldering in N_2 and Air, and with the addition of Nickel micro particles on PCBs/substrates).

In chapter 5 are presented the conclusions obtained from this study, and the proposals of possible future works.

CHAPTER 2

REVIEW OF THE LITERATURE

In this chapter are presented the main concepts related to soldering in electronic industry. First are referenced the Print Circuit Boards in which are presented the principal types of PCBs and surface finishes used in the industry. Then are covered the components, in which are presented some type of components used in the electronic industry.

Secondly are presented the concepts related to soldering, where are: explained the type of solders normally used in the industry; explaining the soldering processes, mainly Reflow process; and the parameters normally utilized; and finally some of the soldering defects that exists are explained.

2.1 Printed Circuit Board (PCB)

Electronic devices resulting from a combination of electronic components connected one to another through a plate named Printed Circuit Board (PCB). PCBs are used in diverse electronic devices, in order to provide mechanical support to the components and electrical connection between them, forming the electrical circuits [6].

In 1936, Paul Eisler made a significant contribution in the electronic industry with the invention of PCBs, and in 1943 he patented this method of etching circuits on a copper layer bonded to a non-conductive base, reinforced with glass. Then the advance of electronic technology, the components became very small, and manufactures reduce the overall size of the PCB and the electronic package [6].

Figure 1. Printed Circuit Board, SolarA after Reflow and Radial process.

PCBs are constituted by one resistant and non-conductive substrate on which are printed the layers, conductor tracks, pads and vias. The substrates generally used are the FR-4 (glass fiber plus resin) and PTFE (commercially known as Teflon) by having a low electrical conductivity, acting as a barrier between the printed electrical conductor tracks [7].

Layers and printed tracks are made of a conductive material normally copper. A simple PCB normally has two copper layers, in the top and bottom of the PCB, but with the advance of technology, PCBs may have more than 2 layers. The electrical connection between these layers are made through a hole in the board, named vias or microvias that are also made of cooper too. Some vias are covered by solder mask to protect them from being soldered [1].

The connection between the electrical component and PCB are made through the pads that are a portion of exposed metal on the surface of a board to which a component is soldered. These pads are terminals made of copper that normally have a conductor surface finish to protect from oxidation, but without damaging the electrical connection. The electrical components can be attached to the PCB by to different technologies:

- **Surface Mounted Technology (SMT)**, where components are mounted, or directly placed, and soldered onto the surface of the PCB. This technology uses more compact components, and higher circuit densities can be used on smaller boards. This is especially important, because today, electronic industry are growing more complex and more compact [8];
- **Through-Hole Technology (THT)**, where the components lead wires are inserted into metallized plated holes that cross completely the PCB and soldered to the walls of the hole. This technology is extremely reliable, as it provides strong mechanical bonds, however, the holes makes the production of boards significantly more expensive. This kind of components are larger, which results in a lower density per area [8].

Finally, PCBs also have a solder mask film placed on the plate in order to isolate the copper tracks from contact with external agents, leaving only discovered the zones to solder, pads for example.

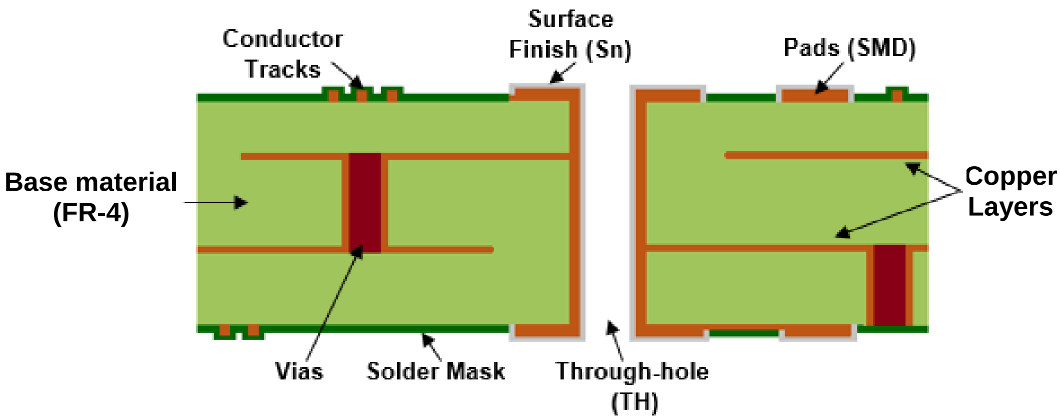


Figure 2. Schematic representation of a PCB.

2.1.1 Classification of PCBs

Printed Circuit Boards may be classified according to the specifications and requirements of the final product, such as automotive and non-automotive applications, but principally based on the number of layers, and type and number of components used. This way, PCBs may be:

- **Single-sided PCBs**, which consists in a board where, all electrical components are fixed on one side but soldered in the other side (figure 3a). This PCBs are used in cases of simple circuits, so the manufacturing costs are low [1];
- **Double-sided PCBs**, also named 2-layer board, is the most common type of board where electrical components are attached to both sides of the substrate (figure 3b). This kind of PCBs have only two layers connected to each other through plated through-holes. Comparing to the single-sided PCBs, these are more expensive because their higher complexity. This is the type of PCB studied in the dissertation (SolarA product) [1, 7];
- **Multi-layer PCBs**, which are similar to the double-sided PCBs, but have more than two layers, because in some situations the necessity of having more density connection, is high to be handled by only two layers (figure 3c). The manufacturing costs depends upon the complexity of this type of PCBs (more complexity, more costs) [1, 7];
- **Flexible and Rigid-Flex PCBs**, which are classified on the basis of the type of material used in the board, flexible material (figure 3d). These flexible boards are very thin (range of 0,1 mm thickness) with copper on both sides in rolls, and are used in application with restriction of space and low weight. The manufacturing costs depend upon the complexity of the PCB, and the materials used to his production [1, 7].

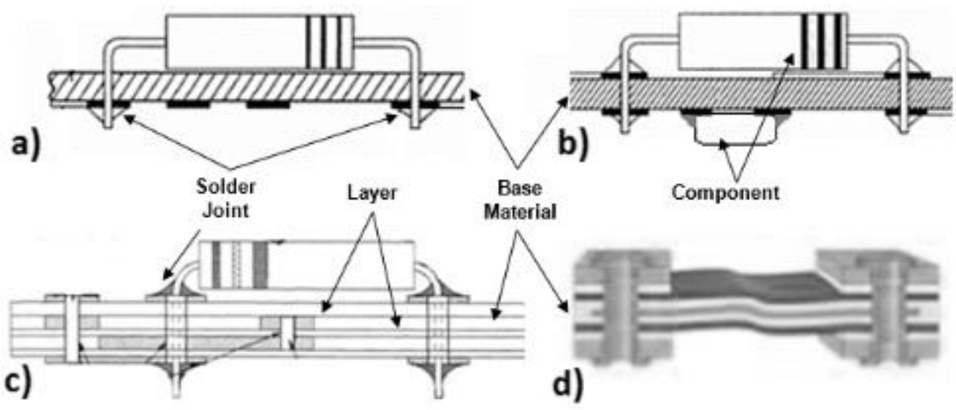


Figure 3. Schematic representation of various types of PCBs. a) single-sided PCB; b) double-sided PCB; c) multilayer PCB [Adapted from [1]] and d) rigid-flex PCB [Adapted from [9]].

2.1.2 PCB Surface Finishes

A surface finish, in a simple explanation, is a protective coating film applied on the surfaces of the PCB, to protect the exposed copper (pads and plated through holes) to preserve solderability and reduce possible defects that occurs after soldering (figure 4). Independent of the coating materials used, they need to guarantee: a good solderability during the soldering process in other to have a reliability solder joint; protect the exposed cooper from oxidation and deterioration until the component assembly, and finally minimize the copper dissolution during the soldering process [10, 11].

Every finish material has their own benefits, but the process, product or environment will dictate the surface finish that is best suited for the application. So, it is important that the PCB designer or assembler work, close with the PCB supplier in order to select the best finish for the specific product. The appearance of the new solders alloys (lead-free) affects the compatibility of the finishes with the metallurgy of the solder joint. This may influence the pad wettability, the plated through holes fill, appearance of voids and others defects that may put in question the reliability of the final product [10, 11].

In the industry many types of surface finishes are used, but the most used and mentioned in the literature, are:

Hot Air Solder Leveling (HASL/Lead-Free HASL): consists in a solder alloy coating (figure 4a) to protect the copper exposed on the PCBs. At the beginning this coated film is composed by a Lead solder (Sn63Pb37) and most surface finish mostly used because the high solderability. This happens because the solder and HASL have the same chemical composition, then "Nothing solders like solder". With the legislation and appearance of the lead-free solders, the soldering process parameters was changed, as the process temperatures [10, 11].

To create the HASL finish, the PCB is bathed in a molten solder that covers all the copper surfaces exposed, then with hot Air knives, the excess solder are removed from the surface. HASL provides a very reliable solder joint, making the component soldering very effective, cheaper and of easily application, and have a long shelf life. But, due to the irregular thickness of the coating this film has poor coplanarity, which can be unsuitable for fine-pitch components [11, 12].

Organic Solderability Preservative (OSP): consists in an organic coating (figure 4b) to protect the copper exposed on the PCBs from the environment until and during the soldering processes, when the PCB suffer more than one soldering process. When this happens, the OSP coating needs to resist the thermal degradation that the soldering process (e.g. Reflow) imposes. For that, this coated film need to have a sufficient thickness to resist this conditions, so the thickness are around 0.2 and 0.5 μm. During the soldering process, the solder temperature or solder flux, can remove /degrade the OSP film allowing the soldering [10, 11].

This surface finish is cheaper and of easily application, but, it is easily degraded by temperatures, and it has a difficult inspection and a limited shelf life [11, 12].

Electroless Nickel/ Immersion Gold (ENIG): consists in a double layer metallic coating (figure 4c), Nickel and Gold, where nickel acts as both a barrier to the copper and a surface which the components are soldered. The Gold layer protects the Nickel during the storage. It is the most popular surface finish in the industry because it answer to major trends such as lead-free requirements and the rise of complex components which require flat surfaces. To prevent the mixing of Au with Cu, and the eventual solderability problems caused by oxidized copper at the PCB surface, layer of nickel is deposited to separate them. ENIG has a thickness about 3 to 6 μm of Ni, deposited by electroless Nickel plating, and 0.05 to 0.125 μm of Au obtained by immersion Gold plating [10, 11].

ENIG has excellent solderability, long shelf time, works well with lead-free solders and has a high consistent thickness. On the other hand, this coating is expensive, cannot be reworked and can cause "Black Pad Issues", which consist in a buildup of phosphorous between the Ni and Au layers that can result in faulty connections [11, 12].

Imersion Tin: consists in a thin coating of pure Tin (figure 4d), with a typically thickness about 0.6 to 1.2 μm, which protects the underlying cooper from oxidation and provides highly solderable surface. This surface finish is produced by immersing the board in a Tin bath (galvanic displacement process), forming an intermetallic with copper that could be a challenge to shelf life [11, 12].

Immersion Tin has a low manufacture cost, a flat surface, good solderability and can be reworked. On the other hand, the thickness is difficult to measure, it can produce a brittle intermetallic, and degrade with time and multiples Reflow soldering, and can occurs solder mask attack (during this coating manufacturing) [11, 12].

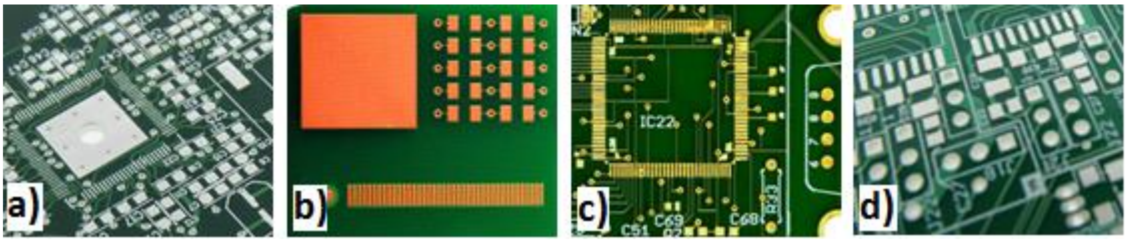


Figure 4. Examples of the most used PCB surface finishes: a) HASL; b) OSP; c) ENIG; d) Imm. Tin [13].

2.2 Components

Electronic components are assembled on the PCB to complete the electric circuit and form a functional and operating system. These components are incorporated in the electric circuit by soldering them to the pads of PCBs, where solder makes an electrical and mechanical connection [14].

Today in the market it is possible to find a great variety of electronic component packages, according to the manufacturing requirements and performance needed for the final product. Then, there are two types of components, Surface Mounted Devices (SMD) and Through Holes (TH) (figure 5). In a simple explanation, SMD are all those components that are soldered in the same side of the PCB, where the component are placed. TH are all those components that have pins (lead wires) intended to be mounted through a plated hole, and are soldered to the opposite side of the board from which the component was inserted (normally mounted in just one side of the PCB [8, 15].

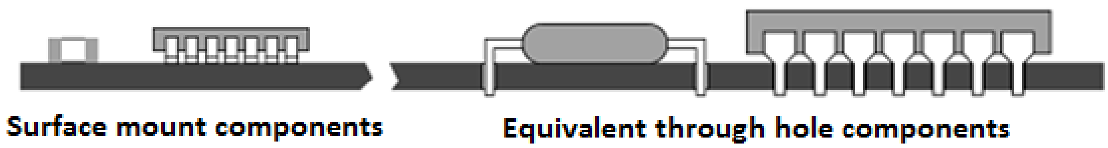


Figure 5. Schematic representation of the types of components that exist, SMD and TH [8].

Actually, in the electronic industry the tendency is to replace most TH components by the SMD because the development of the technology and the emergence of complex and small electronic products. This way, comparing SMD with TH devices, these are:

- Smaller than TH type, allowing the design of smaller and denser PCBs, and enable applications that would be impossible with TH components;
- A type of components which can be mounted on both sides of the PCB (if necessary), and their placement and processing lends themselves to fully automated assembly, reducing assembling costs [8, 15];

On the other hand, SMD have some disadvantages when compared with TH, which are:

- High investments on machinery because of the need of an automatic production;
- Some large components like the higher-power components, can't be SMD type;
- Soldering processes with higher parameters and restrictions, which may lead to occurrence of more defects. It's harder to test and rework SMD boards comparing with TH [8, 15].

In figure 6 are presented some examples of SMD and TH components mostly used in the industry, and at Bosch Car Multimedia product (SolarA) used.

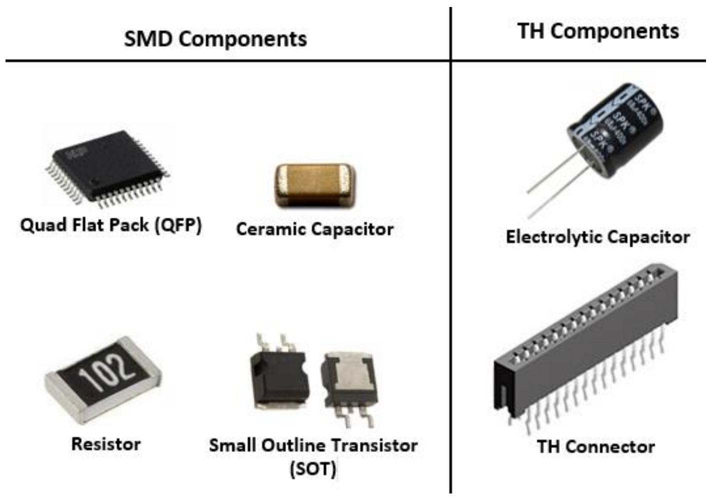


Figure 6. Examples of SMD and TH components used in SolarA product.

2.2.1 Components Metallization

The electrical components have to be attached to the PCB during soldering, so, for this, the components lead material must be electrically conductive, and have affinity with the solder. The most common material used in components leads is copper, and as it is known, this material is susceptible to oxidize by the environment, time and principally by the number of thermal cycles which the components are subjected. So, to protect and minimize these effect of the components leads (pins) some kind of protection is needed to be apply, in other to assure solderability during soldering.

Like PCBs, the solution to this problem is to apply a barrier that protect the surface to solder by applying a protective layer to the components leads (metallization) [14].

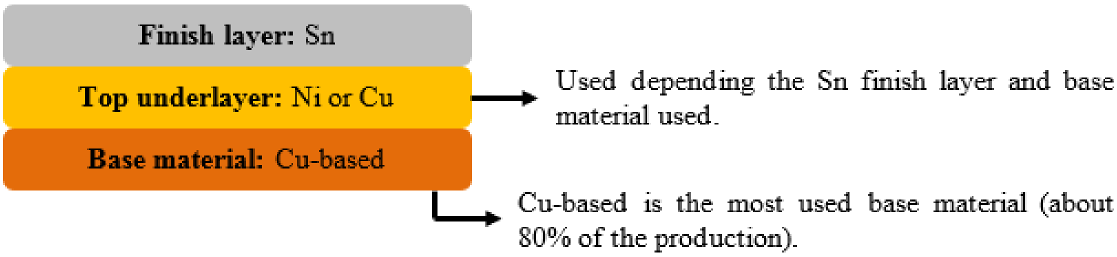


Figure 7. Scheme example of the electric components metallization.

In the electronics industry, as in the case of Bosch, the majority of the components have a copper base material (about 80% of all products), but according to the type of component or the specifications of some products, other base material (e.g. FeNi) can be used. To protect this base material, the most used finish layer utilized is Sn, and according to the final product application, this layer can be applied with different thicknesses. Lastly, there are components, which according to some requirements and to avoid some defects, need to have an intermediate layer of Ni or Cu (between Cu-based and Sn layers) [16].

2.3 Introduction to Electronic Soldering

Soldering is a technology that has been used for thousands of years, as in the Roman times where they made solder connections of the aqueducts pipes with a mixture called tertiatium [17]. Actually, soldering has been used in many applications, but with the emergence of electrical technology, it takes an important role in the electronic industry [18].

This way, soldering is a technique used to join two materials together using a filler (the materials normally used are metals). The connection of these metals are made by a filler molten alloys with melting temperatures below 450°C, where this alloys are a mixture of two or more pure metals with lower melting point than the metals to solder. The molten solder need to be capable of wetting the metals to solder, forming an interphase (intermetallic) near to the joint where the microstructure is altered, and solidifying creating a conductive and resistant bond between them [17, 18].

To the Printed Circuit Boards soldering, is using low-temperatures filler metal, which is usually a tin-containing alloy. In order to have the wettability obtained at a temperature of 450°C, but using low-temperatures (about 183°C to 220°C), a fluxing agent is used, also called flux. This flux assist the wetting on the basis metal by dissolving the oxide film present and clean the interface to solder [18].

So, during the soldering process the molten filler metal reacts with a small amount of the base material (normally copper pad) and the component lead, forming an intermetallic compound. After soldered, the component is expected to be attached to the PCB, through a solder joint that connects the component leads to the PCB pad. At figure 8 is shown a schematic of what is obtained after a soldering process [17].

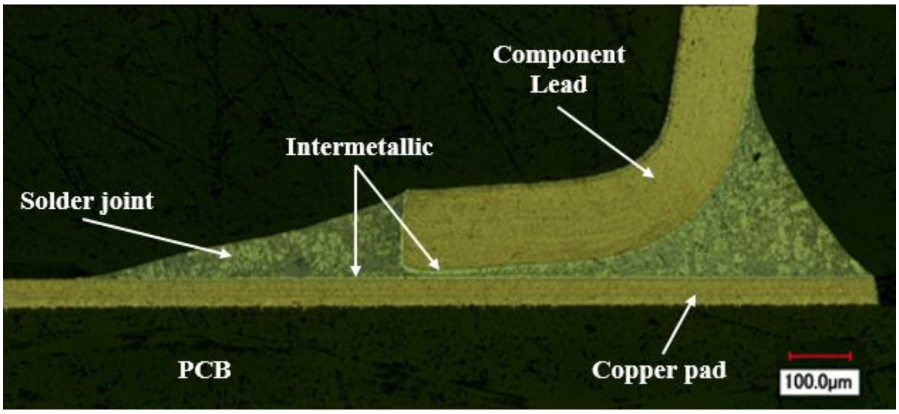


Figure 8. Constitution of a solder joint (SMD component – lead of a QFP).

A few years ago, the soldering processes utilized eutectic or near eutectic solder alloys of Tin and Lead (63wt%Sn – 37wt%Pb), which begin to melt at 183°C. But now, due to the legislation that forbids the use of Pb solders, appear the Lead-free solders (solders without Pb). These Lead-free solders requires higher process temperatures, so, may be necessary to change the components, PCB boards and even process equipment's. This way, it should be taken into account the process parameters and control the process window [19].

2.3.1 Soldering Basics

In soldering it is necessary to take into account some concepts to obtain the best solder joint possible, which depends strongly on the combination of filler and component materials (surface coatings), and also the process conditions used.

To occur soldering it is necessary that the solder has to be in contact with materials to solder, like component and pads of the PCB. The spreading of the solder on the surfaces to solder, is influenced by wetting and surface tension effect, and it must have good solderability in other to form an interphase, intermetallic, resulting of the chemical reaction of the solder with the surface to solder. [19].

Wettability is defined as the tendency of a fluid to adhere or spread over a solid surface, establishing a contact angle which results from the balance between adhesive and cohesive forces. The liquid phase will spread over the solid surface until the three surface tensions: between the liquid and the solid surface (γ_{SL}); between the liquid and the atmosphere (γ_{LV}); and between the solid surface and the atmosphere (γ_{SV}), are in balance, according to equation 1.

$$\gamma_{SL} = \gamma_{SV} - \gamma_{LV}.cos\theta \qquad \text{(Eq.1)}$$

According to this equation, the contact angle θ provides a measure of the quality of wetting, in other words, if 90° < θ < 180°, some wetting occurs but the liquid won't spread on the surface. So, the smaller the contact angle, θ < 90°, better will be the wetting and spreading over the area to solder (figure 9) [20].

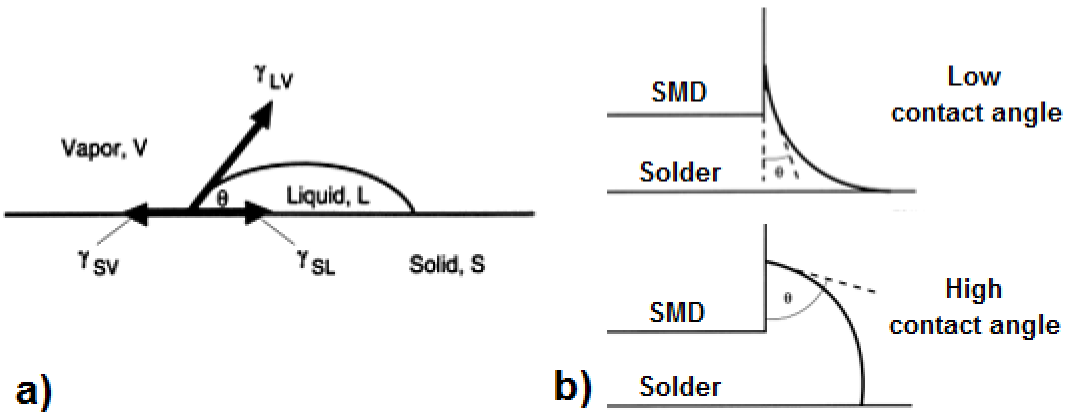


Figure 9. a) Surface tension forces according to the classic model of wetting; b) effect of the contact angle on fillet formation and geometry [adapted from [20]].

Wettability and spreading can be affected by parameters such as temperature, time and metallurgical and chemical nature of the surfaces. High temperatures increase the atomic activity, the reaction rates and the fluidity of the liquid solder, which results in a better wetting. In the other hand, higher promotes the formation of oxides. Time is important, because it is necessary to have time to occur solder-substrate interaction. In other words, it is necessary time to reach the necessary heat conditions, to flux action, to initiate wetting and time to spreading occurs. The nature of the surfaces affects wetting and spreading, because some surfaces are easily wet than others. The presence of oxides, oil and silicone or other type or residues need to be cleaned to not interfere with wetting. The coating films to protect from oxidation, like OSP can be a problem to this phenomena too [17].

Solderability is defined as the ability of a metal to be wetted by a molten solder, and it depends on the wettability of the two surfaces to be joined. This phenomenon is important to have a reliable solder joint, to use less active fluxes (less aggressive), and finally to obtain a greater solder fillet geometry and resistant to mechanical stresses [17].

During the storage and soldering process, solder surfaces can oxidize especially in an Air atmosphere, so this is a problem that reduce solderability. This way, it is necessary to find a solution to reduce or eliminate this problem. Then, the solution found to this oxidation problem is the application of a chemical agent, flux, during the soldering process [19].

Soldering Flux is a liquid or solid material which, when heated are capable to promote wetting by removing tarnish and oxidation [19]. It also acts as a barrier preventing from re-oxidizing of the melted solder, and has to ensure that it flows over the surfaces to be bonded without interference of the oxide layer that may form during the process (figure 10). Fluxes need also to be harmless to components to solder, be easily removed and thermal stable at the process temperatures [21, 22]. But due to the flux be in the solder paste or be directly applied to the surface of the PCB, the oxidation problems may be more problematic in the components pins (leads). This can happen because the flow cannot act in full on the surface of the solder pins.

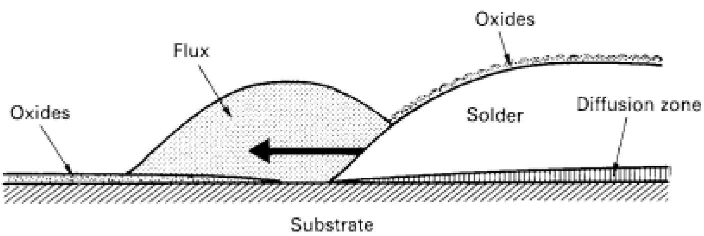


Figure 10. Schematic of the function of the flux in soldering [adapted from [22]].

Several types of fluxes are available in the industry, but only two broad categories are most used. One is the clean flux, also known as water-clean flux, which is composed of relatively strong organic acids and may be fortified with halogens to increase its chemical activity. This type of flux need to be washed from the surface printed circuit assembly after soldering, to avoid corrosion and electrical failure. The other type of flux is rosin-based, with additives to change the characteristics of the flux, increasing is activity and aggressiveness. To remove this type of flux from the printed circuit assembly some solvents are necessary, but as the resulting residues are inert, they can remain on the board surface, called the no-clean fluxes [21, 22].

Even if guaranteed the process ideal conditions, and absence of possible factors which influence the solderability, it must be ensured that, exists the formation of an interphase between the solder and the surfaces to solder (PCB and components), named intermetallic compound (IMC).

Intermetallic is a layer created at the boundary of the liquid solder and the solid surfaces (diffusion zone). The intermetallic is the key to soldering, because without IMC, there is no solder joint. So, for this layer to be formed, the metal surfaces need to be metallurgically compatible with the solder to create the interphase which holds them together (figure 11). The volume of the intermetallic compounds formation, depends essentially on temperatures and time during the process, and during its formation, the base metal dissolves in the molten solder in a quantity that depends on its solubility in the solder [17, 19].

Intermetallic compounds are more like a chemical compounds than metallic alloys, and they act like a glue that forms the structural bond between the solder and the surface metals to solder. But this layer can cause several problems because:

- It is a brittle material that decreases the mechanical reliability (liable to crack);
- They generally have poor electrical conductivity comparing to solder and base materials [17, 19].

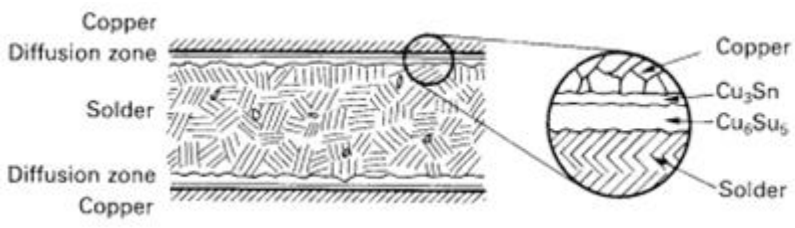


Figure 11. Schematic cross-section of a SAC solder joint – Intermetallic compound [adapted from [22]].

For Bosch, as the goal is to reduce the maximum production costs (e.g. the energy), the process window is set to form the as soon as possible between the intermetallic between the pad-solder and solder-component, no matter their thickness.

2.4 Solders

Solders are metals or metallic alloys normally used to join metallic surfaces as in the case of electronic industry. To form a solder joint, these metals alloys have to be melted and have a melting point below that the metallic surfaces to join [23]. These solders can be provided in two ways, in wire or solder paste, according to the type of soldering process used. Manual and Wave soldering normally use solder in wire form. In the case of Reflow soldering is utilized solder pastes, which consist in small solder particles with dimensions in the range of 5 – 75 μm [24], mixed in liquid flux.

Solders used for electronics are normally made by a combination of Tin and other elements in different proportions, and is possible to find various types of solders available in market. Solders aren't made only by Tin, because the cost comparing to other materials is higher, and higher Tin contents in solders can have limited applications and less proprieties [25].

During the years, electronical industries used the Sn-Pb (Sn63Pb37) solder, due to its high solderability and low melting point (183°C), comparably to other solders. These solder is a eutectic solder, because according to the Sn-Pb phase diagram, to this two elements ratio, the solder changes from liquid to solid directly at 183°C, without an intermediate phase (plastic phase) [26].

But from 2006, the solders with lead began to be forbidden due to environmental concerns (toxicity to the environment and human being) according to European Union's Restriction of Hazardous Substances (RoHS) Directive and Waste Electrical and Electronic Equipment (WEEE) Directive. Then, to substitute the Lead solders, began to emerge the first lead-free solders (solders without Pb in their composition) in industry [4, 5].

Lead-Free solders have similar properties as lead solders, but presents differences like higher melting point and surface tension and do not wet or spread so good as the Pb-solders. In practice the main problem of the lead-free solders is that their melting temperatures are not as low as Lead solders. Pb solders melts at 183°C and Lead-Free solders melts in the range of 217 to 229°C, according to ratio and composition of each solder [5, 26].

2.4.1 Types of Solder

With the development of electronic industry, the requirements are higher, so it's necessary to find new solutions to respond to these necessities. With the reduction size of the electronical devices, the components packaging and density on the PCB makes that the available areas to solder are increasingly small. This way, the probability to occur defects, combined with the existing problems of oxidation during the process, requires the existence of specified solders for each application [1].

Since the Lead solders left the market, many types of Lead-Free solders starts to appear in the industry, as it is possible to see in figure 12. So according to each soldering requirements, there are solders with different compositions and ratios capable to soldering in Air atmosphere, with lowest temperatures, no-clean solders, among others specifications.

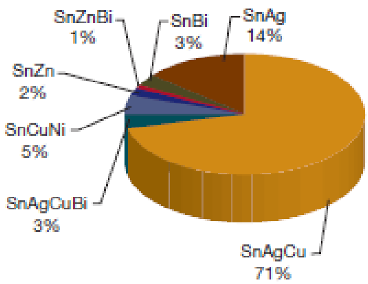


Figure 12. Principals Lead-Free solders used in Reflow process - *European Lead-Free Soldering Network, released March 2007* [adapted from [27]].

According to IPC norms, the family of Tin-Silver-Copper alloys, denominated SACs, are the solders recommended in the electronic industry, as the replacement for the lead solders. Since Pb solders were forbidden, SAC solders became the industry standard. The SAC most used are SAC305 (96.5Sn – 3.0Ag – 0.5Cu) and SAC405 (95.5Sn – 4Ag – 0.5Cu), which, according to the Sn-Ag-Cu phase diagram, are near to the eutectic point, characteristic of a melting point about of 217°C (figure 13). From all the existent Lead-Free solders, these two are the ones with the closest properties to the Pb solders [25, 26].

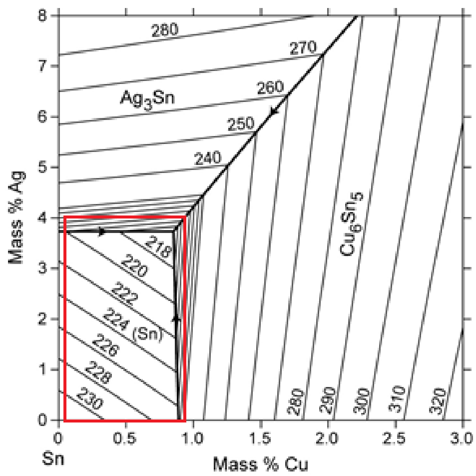


Figure 13. Section of the ternary phase diagram corresponding to SAC solders compositions mainly used in soldering (marked in red) [adapted from [28]].

It's very important to consider the microstructure during the fabrication, because small changes in the composition can lead to a large differences in microstructure. In order to avoid this problems and possible defects during the soldering process, the solidification behavior needs to be studied [25, 26]. But these solder alloys have also the advantage of modify their composition, by adding other elements, in order to improve their properties. Then, this is possible by adding alloying elements, like Zinc, Aluminum, and Bismuth for example, to study their effects on SAC alloys [26].

2.5 Solder Alloying Elements

Since Pb-solders, solders with identical properties have been used, Lead-Free solders. However, many problems of these solder alloys (especially SAC) still exist, such as the higher melting temperatures, less wetting than Lead solders, large brittle intermetallic and high costs [29]. This way, with the development of soldering industry technologies such SMT fine-pitch design (the fine spacing between the pin leads, spacings of 0,65 mm or less [30]), as well as the increasing environment requirements, is necessary to investigate and create new Lead-Free solders with better proprieties [29]. In order to enhance the properties of Lead-Free solder alloys, elements such as Bismuth (Bi), Indium (In), Gallium (Ga), Zinc (Zn), Nickel (Ni) among others, can be selected to be added into these alloys [25, 26, 29].

There are many methods to intervene in the solder to obtain the final properties expected, such as better wetting, spreading, lower melting temperatures and finally the mechanical strenght of for the solder joint. One of them consists by adding micro or nanoparticles, which does not involve a diffusion process and the production of a new alloy, but participation in the solder system [29, 31].

For this, in this dissertation will be studied the effect of adding micro particles of Ni into the flux, which will be placed before the soldering process.

Nickel:

In literature, it is possible to find that Ni has already been subject of study as an alloying element in some solders, and also studied the influence of adding in micro or nanoparticles in the solder. This way, it is possible to know the properties of a Lead-free solder when adding Ni.

According to some research made, it was seen that when adding Ni in the alloy form into Lead-Free solders, it:

- Influence the morphology and thickness of IMCs, when added in the form of nanoparticles or as an alloying element addition [32];
- Improve mechanical properties, and provide a diffusion barrier between Cu and Sn based solder alloy, in order to prevent, or at least suppress the formation of the Cu_3Sn phase [33];
- Decrease the wetting force [33], increase the wetting angle [32, 34, 35] and have longer wetting time [34].

When it comes to adding Nickel shaped particles, micro or nanoparticles, the effects on the final properties are slightly different. According to the literature, when the nanoparticles are added within the solder flux, the diffusion process is different with the presence of nanoparticles of Nickel, so they block the formation of voids. The Nickel particles are also capable to increase the shear strength of the Lead-Free solders [36].

When the Nickel particles are added into the solder paste, during the soldering process (e.g. Reflow), the intermetallic grow between the copper layer and solder, but also around the Ni particles in the form of "sunflower" (figure 14), named the sunflower shaped intermetallic particles [37, 38, 39]. This type of solder paste with particles of nickel, seems to produce no major changes in terms of wettability, comparing to the existent Lead-Free solders [40].

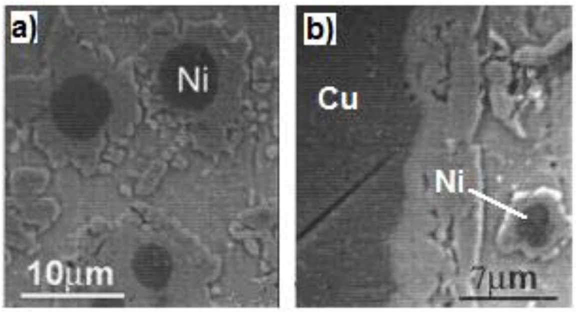


Figure 14. Effect of Reflow on the growth of intermetallic layers (sunflower): a) around the Ni particles b) at Cu substrate/solder interface with Ni, [adapted from [38]].

However, for this dissertation, the purpose of adding Ni micro particles is to evaluate their influence at the soldering process, in an inert and oxidant atmosphere, and expect to achieve better results.

2.6 Soldering Atmosphere

With the increasing of density and high performance of electronic devices, components are increasingly smaller, taking to a reduction in solder joint dimensions. As already mentioned, the solder joint has the function to conduct electricity and create a mechanical joint. This way, during the soldering process, it must ensure that there will be a good wetting and spreading, without presence of other defects that may call into question the solder joint reliability [3, 41].

2.6.1 Air Atmosphere

The main problem which can promote a bad soldering is the creation of oxides (non-solderable surfaces) in the zones to be soldered. This happens principally because the natural heat of the soldering process combined with the oxygen present on Air (about 210 000 ppm O_2), oxidize solder and the surfaces to solder, pads of PCBs and the pins/leads of the components [42]. One the other hand, during the soldering process, beyond the temperature and the oxygen concentration, oxidation is effected by the surface area, flux content and metal type/content [43].

Oxidation is directly related to:

- Higher temperatures, because higher temperatures means faster rates of oxidation. Thus, to reduce the rate of oxidation it is needed to reflowing at the lowest possible temperatures [43];
- Oxygen content and Air velocity, because the greater the concentration of oxygen in the Air, more likely to oxidize. With forced convection in the oven, the greater the amount of oxygen from particles which come into contact with the solder, increasing the oxidation [43];
- Surface area, because with more exposed area, means more area available to oxidize. This refers to the pads/leads to be welded and the solder particles in the paste, because the smaller they are, it has more are exposed. This situation happens more often with the use of fine-pitch technology, because leads became finer and finer [43];
- Metal content, because some metals are more solderable and propitious to oxidize than others. This way, surface metals need to have a coating to protect from oxidation, during the storage and all the soldering processes applied [43];
- Flux activity, because to remove oxides is necessary aggressive fluxes, more activity. The no-clean fluxes contains a smaller amount of activators to reduce residues that remains on the PCB, however, with this reduced flux activity the oxidation may be a concern [43]. The

residues resulting from the reaction of the flux with oxides, have a brown or yellow coloration, which may disturb the inspection of solder joints [42].

Table 1 shows the variables, mentioned above, that effect oxidation.

Table 1. Variables that effect oxidation in Reflow soldering process [adapted from [43]].

Oxidation variable	Variable trend	Reflow result
Temperature	Higher	Worse
Air velocity	Higher	Worse
Oxygen Content	Lower	Better
Exposed Area	More	Worse
Metal content	Non-Tinned	Worse
Flux activity	Lower	Worse

To avoid this oxidation problems, the solution may be to use an inert gas for the local atmosphere [42].

2.6.2 Nitrogen Atmosphere

Nitrogen (N_2) is an inert gas very used in industry due to its properties and to be unreactive at standard temperature and pressure. It is used in electronic applications, such automotive industry due to high quality and reliability that this gas can promote in solder joints. It is the most used inert gas because it is the cheapest available gas, about 78% of the Air composition, which does not react with metals, preventing their oxidation [3, 44].

Nitrogen atmosphere used during the Reflow process is known to improve the soderability by preventing oxidation of the surfaces to solder, improving the wetting and the reliability and quality of solder joints. Comparing to an oxidant atmosphere such as Air, Nitrogen can widen the process window of reflow soldering, reducing effectively the number of defects that possible can occur [44, 45]. The using of Nitrogen allows the utilization of No-clean fluxes, because the residues production are very low making the inspection of solder joints on finished PCBs easier [42].

However, Nitrogen have some negative points that must be considered like the high costs and tombstoning. This last defect, happens when using too much Nitrogen during the Reflow, so, having only a Nitrogen atmosphere, may bring defects [42]. This happens because, as PCB advances in the oven the part that goes ahead heats first, and so do the components. This way, the solder wet around the one and, the surface tension of the molten solder on that wetted end results on the lift of the component before the solder paste goes molten and wets the other end. So this defects is most often seen on the smallest devices, as SMD Chip Capacitor and Resistors [42].

Then, to reduce this and some other defects, the atmosphere must be controlled and maintained an acceptable oxygen concentration to obtain a desired or best soldering performance. With some oxygen levels during the Reflow, the surface tension of the molten solder may decrease and the component do not lift. For this, and according to literature, the concentration level of oxygen may be about 1000 to 1500 ppm O_2, to minimize tombstoning and obtain the best solder joint possible [3, 42].

Finally, even with the advantages of using Nitrogen, due to its high price, it is always questioned whether the use of Nitrogen as the atmosphere in the soldering process is profitable. For this, all companies must evaluate the yield and costs associated with using this type of atmosphere [44],

2.7 Soldering Processes - Reflow

There are several methods for soldering, but with the advance of the electronic industry it is needed to produce in a large scale. This way, when a PCB is soldered a mass soldering techniques are required. The two most common for these high-volume manufacturing, are Reflow soldering and Wave soldering [2]. The soldering method is chosen by the types of components and PCB to solder, and the requisite solder joint proprieties. Sometimes, in accordance with the functionality and complexity of the products, it may be necessary to apply one or two reflows (the second only if necessary), and finally wave for solder the bigger and complex components [46].

In the industry for the production of an electronic product, the soldering process involves basically the following steps (figure 15):

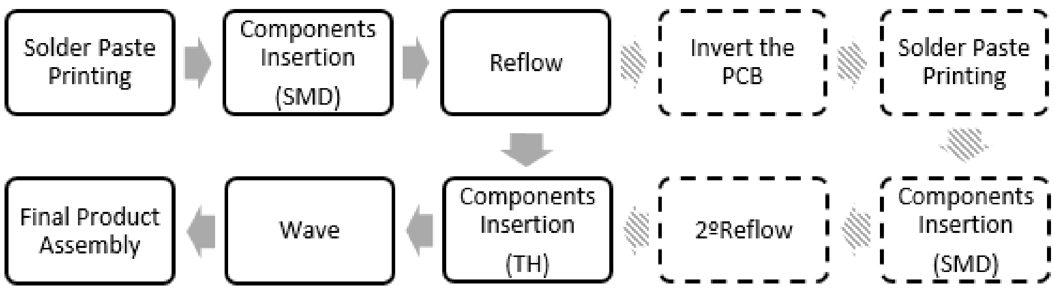


Figure 15. Typical steps used for producing a product, since the single PCB to the final product (Bosch example).

As Reflow process is the main study in this dissertation, will be explained in detail ahead, here is a brief description of the Wave process which is not utilized.

Wave soldering is a large-scale soldering process which consists in using waves of molten solder to attach and solder components to the PCB. The process consists in first, inserting or placing the components into the PCB, than the loaded PCB passes across the top of a tank with molten solder with pumped waves. This way, the solder wets the exposed metallic areas of the board, those ones which are not protected with solder mask, creating an electrical and mechanical connecting [47].

Wave soldering is applicable to wired components (through-hole type) and SMD components too (minimum pitch 0.65 mm). However, these surface mount components need to be placed and glued to the PCB surface before being run through the molten solder wave [47].

The main stages of the reflow soldering process will now be described.

2.7.1 Solder Paste Printing

Solder Paste Printing is one of the first steps of the production, and it is very important because the reliability of the solder joint depends on it. In this step the PCB enters the printing equipment, the line stops and the solder parte is deposited at the points on the upper side of the PCB where the electrical and mechanical connection between the components and PCB are made. The deposition of solder paste onto the PCB contacts is achieved by applying pressure by passing a Squeegee over a stencil, then the solder passes through the stencil openings and it is printed on the pads. The stencil openings geometry must be accurate and match with the pads of the PCB. Each type of PCB have their own stencil [48, 49].

The solder paste is put on the stencil manually, and recharged by the line operator, and must be stirred for about 30 seconds in a homogeneous way, before placed on the stencil. So that the solder paste does not lose their properties, it should have a maximum of 8 hours of work on the stencil. The solder paste homogeneity, surface tension, Squeegee pressure, stencil thickness, alignment and distance between the stencil and PCB, temperature and humidity, are very important parameters to take into account to obtain a reliable solder joint [48, 49].

Figure 16 shows the solder paste printing equipment used at Bosch Car Multimedia Braga, and a surface printed PCB.

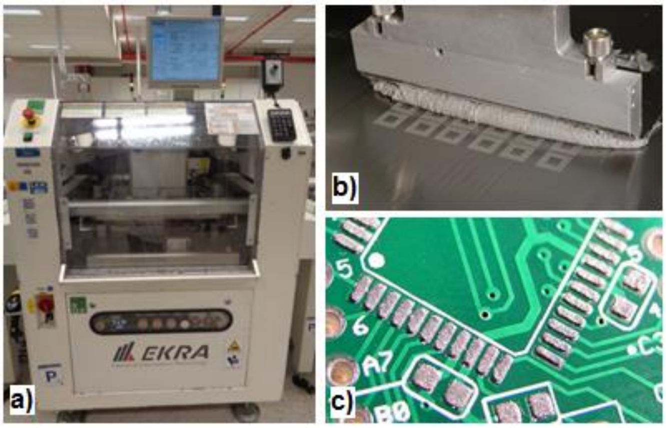


Figure 16. Bosch Car Multimedia: a) solder paste printing machine, EKRA; b) Stencil, solder paste and Squeegee; c) surface printed PCB.

2.7.2 Components insertion

The components insertion is the step that follows the solder paste printing, which consists in placing the components on which the solder paste was already placed. The components are placed on the surface of the PCB by means of automatic machines through a process called pick-and-place. The components are removed from the feeder through a nozzle, placing each component in the intended place of the PCB [48, 50].

The placement of the components should be as fast as possible (about 25000 components/hour) in order to avoid possible defects caused by long exposure of solder paste to the Air. Another parameters that must be taken into account is the placement accuracy and pressure of component placement, in order to not cause excessive solder spreading and damage the components or PCB [48, 50].

Figure 17 shows the components insertion equipment used at Bosch Car Multimedia Braga.

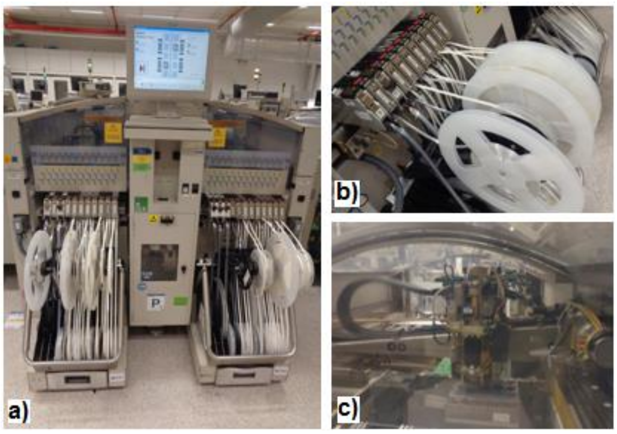


Figure 17. Bosch Car Multimedia: a) components insertion machine, SIPLACE; b) Components feeders; c) nozzle.

2.7.3 Reflow Soldering Process

Reflow soldering is a large-scale soldering process which consists in soldering the components previously mounted in the solder paste, by application of heat in a controlled atmosphere (usually Nitrogen) [51]. A typical line used in the industry, as Bosch Car Multimedia, for single and double side Reflow soldering, is shown below in figure 18. The basics of this process is: application of the solder paste on the pads of the PCB; Placement of the components in the paste, already printed; and finally applying heat which causes the melt solder melt (Reflow), wet the PCB pads and promotes the solder connection [46]. Among these steps there are inspections for printed solder paste (SPI) and at the final of the Reflow (AOI) [51].

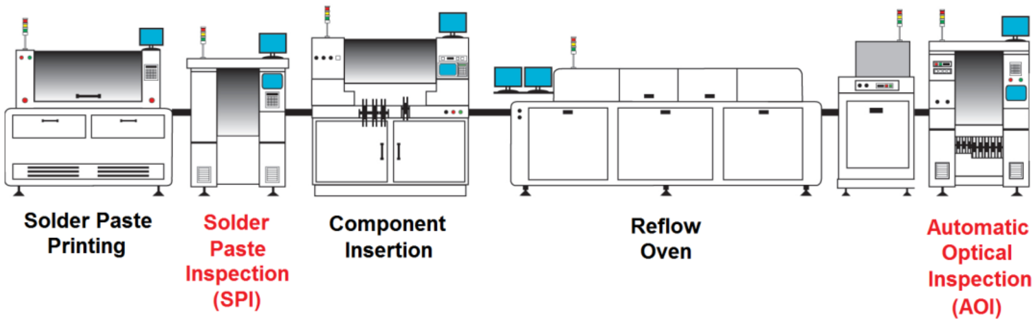


Figure 18. Typical Reflow soldering line used in Bosch Car Multimedia [adapted from [52]].

The most commonly Reflow methods used in industry to massive productions are the, infrared Reflow, Vapor phase Reflow, Convection Reflow and finally the In-line-conduction Reflow. But, beside these methods generally not for high volume production, are also exist, such as laser Reflow, Soft Beam Reflow, Hot-bar Reflow, Collet soldering and resistance soldering [48].

In this dissertation the Reflow process used was the Convection Reflow, which utilizes forced heated convection of a gas in all zones of the heating chamber (figure 19). This chamber is divided in multiple heating zones, which the temperatures are different and controlled. The PCB after enter the chamber, is heated essentially by the heated gas that is forced through the panel, and the heating also have some contribution from the chamber resistances, which heats the chamber and gas. At the industry the gas common used is Nitrogen for the reasons previously explained [48, 51].

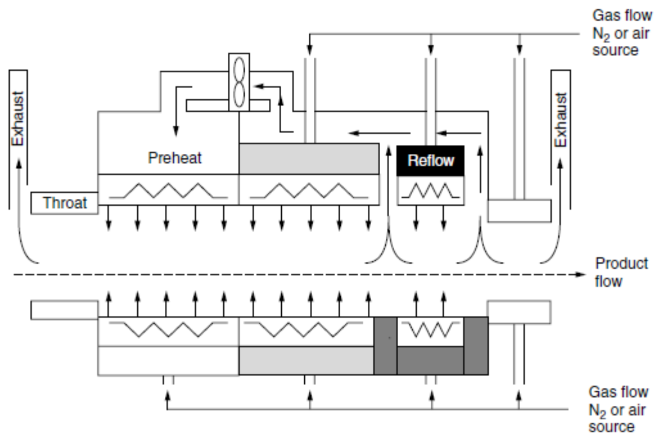


Figure 19. Convection Reflow oven design [adapted from [48]].

The Reflow temperatures must ensure the flux activation, melting of the solder paste, wetting the surfaces to be joined (pads and leads), and solidifying the solder to obtain a reliable solder joint. This way, in order to obtain the best possible soldering, is used a common thermal profile for the Reflow process, which is divided in four important zones/stages: Pre-heat, Soak, Reflow and finally cooling (figure 20) [48].

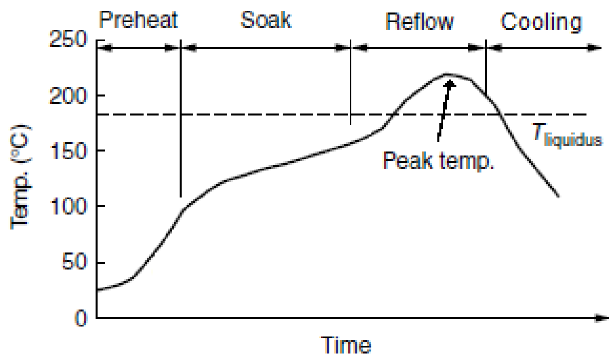


Figure 20. A commonly used Reflow thermal profile – SnPb solder [adapted from [48]].

The control of these zones are very important because the thermal profile varies depending on the products, and solder used, so each zone/stage consists:

- **Pre-heat stage:** in this stage the PCB should be preheated prior to solder Reflow to avoid thermal shock. During this stage the solder paste begins to dry and the solvent and volatiles are allowed to evaporate [48, 51];
- **Soak stage:** in this stage, also known as the flux activation, the temperature reach the melting point of the solder paste, and the flux can clean the bonding surfaces removing the existent oxides. At this stage the temperatures of the PCB surface and solder should be homogeneous [48, 51];

- **Reflow stage:** in this stage the temperature should be increased to the appropriate peak Reflow temperatures (above the solder liquidus temperature, in a range of 20 to 40°C), the exposure time at peak temperature must be controlled to not damage the electrical components. The solder has the condition to wet the surfaces to connect, and starts to forming the intermetallic. The stage time should be sufficient to create the weld joint, and minimal to avoid possible soldering defects. Then the temperatures starts to reduce [48, 51];
- **Cooling stage:** this is the last stage of the thermal profile and consists on the decreasing of the temperature until about 40°C. The cooling of the PCB needs to be gradual, to avoid thermic shock and possible defects. During this period the solder solidifies forming the solder joints [48, 51].

2.8 Soldering Defects

In any manufacturing industry defects are always a problem because they exist and will always exist. With increasing complexity of the electronic products, its production is more liable to acquire from defects. These defects may be related to raw material, the solder, the PCBs, and the components, or related to the soldering process. The defects of the raw material are usually contaminations, or any other disability that might call into question its functionality.

The defects that normally appear on electronic industry, already are quantified and specified in the standards that can be universal or internal to a company. In the case of Bosch Car Multimedia, the current standard used is IPC-A-610, which is a document which presents the acceptance requirements for the manufacture of electrical and electronic assemblies. So, this documentation specify the criteria defined to accept or reject the product. According to each criteria it is possible evaluate the problem and say if it is a defect or not. This way the criteria are divided in three classes [53]:

- **Class 1 - General Electronic Products**: which includes products which the major requirement is function of the completed assembly [53];
- **Class 2 - Dedicated Service Electronic Products:** which includes products where continued performance, extended life is required, and which the end-use environment would not cause failures [53];

- **Class 3 – High Performance Electronic Products:** which consist in products that the downtime cannot be tolerated, and must function when required even in aggressive environments [53].

Several existing defects in the electronic industry, but some of the defects that appear in Reflow soldering process are:

- **Tombstone:** happens when a chip or resistor component that has partially or completely lifted off one end of the surface of the pad. Can caused by poor or skew placement of the component which will create imbalance wetting force on both pads [53].
- **Voiding:** empty spaces within the solder joint, which can be caused principally by the outgassing of flux entrapped and/or excessive oxidation [53].
- **Solder Balls:** Small spherical particles with various diameters are formed away from the solder joint, and can caused: by fast ramp-up or insufficient preheat time that allows the solvent to vaporize; trapped moisture may result in explosive vaporization; or solder paste stuck under the stencil that can be transferred to the components [53].

At figure 21 is shown the defects explained above in a real case.

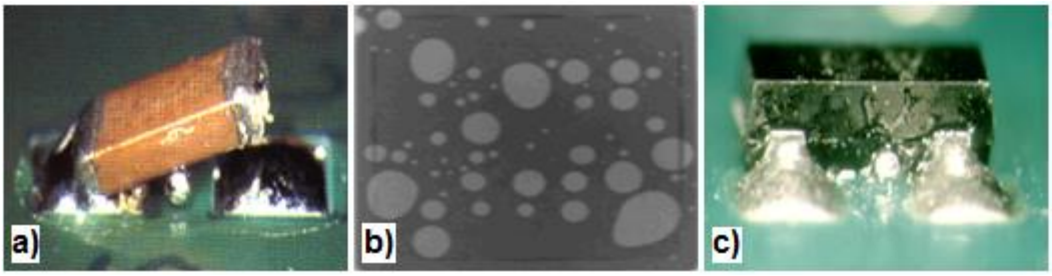


Figure 21. Some SMD soldering defects: a) Tombstone; b) Voiding; c) Solder Balls [adapted from [adapted from [51]].

CHAPTER 3

MATERIALS AND METHODS

In this chapter are presented the materials, the processing methods, the inspection and qualifying techniques and the characterization of the products studied at Bosch company and at the University of Minho, as well as, the experimental procedures needed to develop each technique.

This chapter is divided in four sub chapters, namely, the materials used for this project; the processing methods used in the company and the university, and their procedures; the inspection and qualifying techniques used at Bosch Car Multimedia to evaluate the product; finally the characterization techniques used at the company and university to analyze the obtained products.

For this project at Bosch Car Multimedia were produced, a totally of 328 SolarA PCBs, that were subjected to two different soldering process conditions, as shown at the flowchart bellow (figure 22).

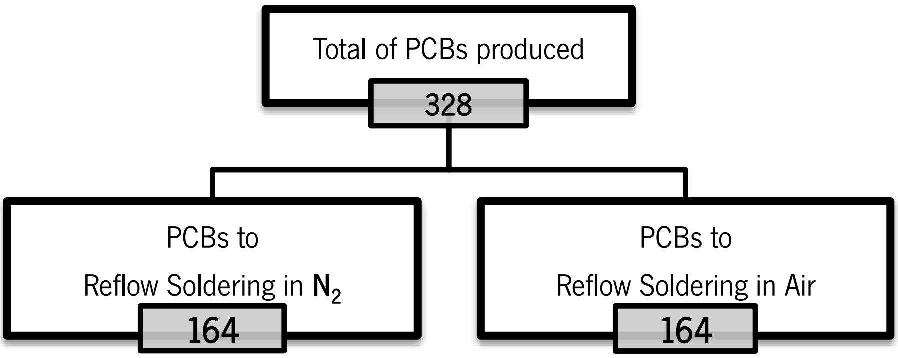


Figure 22. Flowchart with the different soldering conditions used.

The main objective of this part of the project, is to compare the product PCBs soldered with the normal process conditions used at Bosch Car Multimedia (inert atmosphere), with the product PCBs soldered in an oxidant atmosphere.

All the PCBs soldered in these different atmospheres, suffered the same sequence of production. For each group of 164 PCBs solder, is presented bellow (figure 23), a detailed flow chart which shows the type and route of each PCB produced.

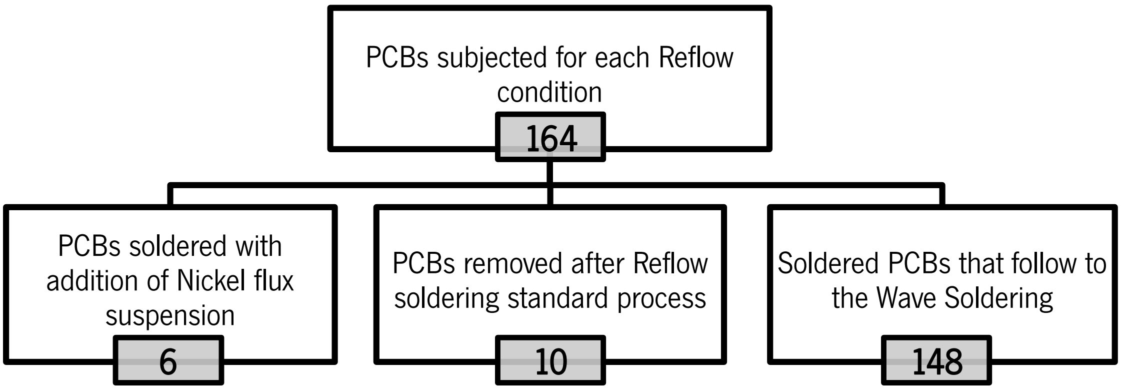


Figure 23. Detailed flowchart about the route of each PCB.

For each Reflow condition (each group of 164 PCBs), were analyzed:

- All PCBs at SPI and AOI;
- 16 PCBs by a detailed visual inspection, at the MFI2-CP department lab, (6 PCBs with Nickel flux suspension and 10 of the removed PCBs after the Reflow process;
- 5 PCBs (without Ni) by X-ray inspection;
- 4 PCBs cut and studied (1 PCB soldered with flux plus Ni, and 3 of the removed PCBs after Reflow). This sampling is reduced due to the reduced available time, and high costs associated of some characterization techniques (as SEM and high costs of the sectional cuts, made at Marques Ferreira chemical lab);
- 148 PCBs after wave will be tested and subjected to reliability tests by MFI2-CP department of Bosch Car Multimedia.

3.1 Materials

This dissertation is divided into two parts, one at Bosch Car Multimedia and other at the University of Minho. At Bosch Car Multimedia for the reflow soldering process, the solder paste used was SAC405 (serie F620), produced and characterize by Heraeus® corporation. The PCBs utilized were PCBs with surface finish of Sn (Immersion Tin) provided by Pacific Fame International Ltd., with the following characteristics:

- *"Nutzen"* (panel) dimensions: 230×185×1.6 mm
- PCBs dimension: 105×137.5×1.6 mm
- Copper layer thickness: 39.68 µm

The components used in the process, correspond to the SMD components normally used on SolarA product, and they were provided by some Bosch suppliers.

At table 2 are presented some characteristics of the two solders used.

Table 2. Solders used at the university to this project.

Solder	Melting Point (°C)	Particle size (µm)	Metal content (%)
SAC305	217	-	100
SAC405	217-219	25-45	88

At University to the experimental tests were used:

- SAC305 and SAC405 solders produced and characterize by Heraeus® corporation;
- Powder of Nickel provided by MERCK®.
- Liquid flux, Cobar 94QMB (REL0) provided by Bosch, to simulate the Wave soldering process use at Bosch Car Multimedia;
- Substrates cut and prepared from a PCB with a surface finish of Sn (Immersion Tin) provided by Bosch Car Multimedia. These substrates had approximately a circular geometry with diameter between 3 and 4 mm, with 1.6 mm thickness, and a 35 µm Cu layer.

At table 3 are presented some characteristics of the two elements utilized.

Table 3. Elements used at the university to this project.

Powder	Particle size (µm)	Melting Point (°C)	Molar mass (g/mol)
Ni	<10 µm	1453 [54]	58.71

3.2 Processing Methods

To study the effects of soldering in an Air atmosphere, several soldering tests, to a real product (SolaraA), were realized in the Bosch Car Multimedia production line. These tests were realized at the production line and was applied only one Reflow thermal cycle, as normally used in this specific product. With the same objective were studied samples of SAC305 and SAC405 at the University of Minho. This work consisted of studying samples soldered at different thermal cycles and different atmospheres, to compare the influence of these parameters in solder joint characteristics.

Then, to reduce the defects resulting of soldering on an oxidant atmosphere, were studied possible solutions to improve the soldering processes. For that, was utilize a solution of liquid flux with Nickel, that was applied on the surface of the PCB or substrate, to evaluate the influence of this Nickel particles at the soldering process in an inert and oxidant atmosphere. These tests were studied in detail at the university, and at Bosch Car Multimedia were tested on the real product SolarA.

3.2.1 Production of Bosch product - SolarA Reflow Process

Soldering in an Air atmosphere, can cause problems like oxidation, then the reliability of the solder may be reduced. So, to study the problems of soldering in an oxidant atmosphere, as Air, and quantify its process window, nothing better than studying in a real product soldered in this different conditions.

To this dissertation was decided, according to Bosch specifications, to study a product produced and marketed by Bosch. For this, the product selected was a non-automotive product (SolarA) because its lower requirements comparing to automotive products and because it is only subject to a one reflow (top of PCB) and one wave (bottom of the PCB) soldering processes. This last requirement was defined according to the minimum number of soldering processes applied to a product, normally subjected to one Reflow and one Wave. So, as this can be the best condition to succeed, this will be the starting point to the study.

The SolarA product samples were produced in a SMD lead-free production line, normally used for this kind of products. The materials, soldering parameters and procedures used in this test, were the same used normally at Bosch Car Multimedia. The solder paste used was SAC405, and the Reflow soldering process was realized in an inert atmosphere (N_2) and in Air.

Experimental procedure:

SolarA product samples were soldered in a Reflow oven, REHM V8 (figure 24), and as the product is only subject to one reflow, it was only necessary to apply on thermal cycle. The thermal profile used, was the standard profile normally applied on the production of this product.

Figure 24. Bosch Car Multimedia Reflow oven, REHM, utilized to SolarA production.

This way, to produce the SolarA product by Reflow soldering process, were taken the following steps:

- Introduce the Reflow soldering parameters, as the atmosphere (with N_2 or Air), temperatures and conveyor velocity;
- Then prepare and put the SolarA PCBs in the entrance of the line, to start the process. The PCBs start to advance automatically through the production line, and first they are marked by laser (barcode) and identified;
- Put and secure that the printing machine always have solder paste, to printing the PCBs, and then they are subjected to a solder paste inspection (SPI);
- Put and secure that the component insertion machine always have components to their assembly on the PCB;
- Certify if all process parameters are according to the initial inputs;
- Finally, after the automatic optical inspection, analyze possible defects detected and accept the good PCBs and reject bad ones.

The temperatures used at the different zones of the Reflow oven, and some others parameters introduced at SolarA production, are presented on the following table, table (4).

Table 4. Temperatures and velocity set in the Reflow oven.

	Temperature (°C)										
Heating zones	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
Top	140	160	170	180	190	200	220	235	245	260	150
Bottom	140	160	170	180	190	200	220	235	245	260	1
Conveyor speed (mm/min)	850										
Atmosphere	Nitrogen with less than 1500 ppm O_2										

At figure 25 is shown the thermal profile that the PCBs is subjected inside of the Reflow chamber. In each zone of the Reflow chamber is measured the temperature, of the PCB, of one SMD component (e.g. chip), of a Body IC (e.g. QFP), of a solder joint of the Body IC, and finally of a SMD component on the underside of the PCB. These temperatures are measured on a standard board already processed, by placing thermocouples at the locations previously mentioned.

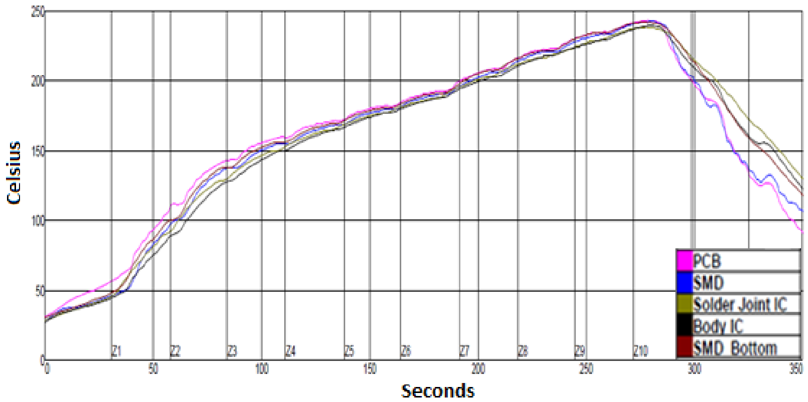


Figure 25. Temperatures registered by thermocouples placed in the standard plate, during the Reflow.

Finally, in order to reduce the soldering defects, at this production line was also performed the tests of soldering with addition of Nickel flux suspension, by pulverization, on the SolarA PCBs surface, before entering the process. These test used the same Reflow soldering parameters, as the atmosphere (in N_2 or Air), thermal cycle and the production line velocity.

3.2.2 Soldering - Adding Nickel into the Flux

A possible solution to minimize oxidation problems found, is the introducing of an alloying element in the flux, in order to try to increase the solder solderability. With Nickel, it is expected that the intermetallic formation could be faster, reducing the Reflow soldering process cycle time. With this, it is also expected that it will be possible the soldering at a lower maximum temperature, compared to those that are already used. This way, it is expected a possible reduction of the energy costs and the susceptibility of oxidation that can occurs.

This way, the solders selected to do this soldering tests, at the university, were SAC305 and SAC405, provided by Bosch Car Multimedia of Braga, and the element selected to adding to the liquid flux was Nickel powder (<10 μm), provided by the University of Minho. The SAC305 solder was provided in wire form, and it was selected because this solder used at Bosch doesn’t have flux integrated unlike SAC405 which is a solder paste, that has flux integrated in the paste.

In order to have a more detailed study, was realized the same test of adding Nickel into the flux, but this time at an industrial scale. The procedure of applying the flux was the same utilized at the university, but this time the PCBs were coated with Nickel flux solution by pulverization. The soldering process parameters utilized, were explained in the previous sub chapter (3.2.1)

Experimental procedure:

To the solderability soldering tests, were taken the following steps:

- Prepared samples of SAC305 cut and polished (with an abrasive paper of 1200 mesh) to obtain samples with approximately the same mass and geometry (1 mm high, 3 mm diameter);
- The PCB substrates (immersion Tin) were cut and polished (with an abrasive paper of 1200 mesh) to obtain approximately the same geometry (3 to 4 mm diameter);
- The liquid flux with Nickel was prepared by mixing Nickel powder into a solution of liquid flux (Cobar 94QMB), in order to get a liquid flux suspension with "2wt% of Ni";
- Finally, were applied a drop of flux with and without "2wt% Ni" on some substrates. After drying were put the solder samples on top of the substrate on each substrate and taken to the TGA-DTA furnace. For SAC405 solder, was tried to add always the same quantity of solder paste on the substrate and proximately the mass of SAC305 samples utilized.

The conditions and parameters used in this test are express at the following table.

Table 5. Conditions used in TGA-DTA to the soldering tests used in the study of adding Ni into the liquid flux.

Samples	Temperature (°C)	Atmosphere	Heating/cooling (°C/min)	Stage at max temperature (s)
SAC305	260 250 240	Argon and Air	30	12
SAC405				
SAC305 with "2wt% Ni flux"	260 250 240 230 220*			
SAC405 with "2wt% Ni flux*				

*only SAC405 + "2wt% Ni" was soldered at 220°C.

3.3 Inspection and qualifying techniques

At Bosch Car Multimedia during the production, each product is subject to some quality control inspections to certify if the product is within the requirements/norms. Most of the times these inspections are made in the production line as is the case of SPI, AOI and sometimes the visual inspection at the end of the line. Other times it's necessary to create samples to effectuate their mechanical and functional evaluation, and check if the process goes according to the parameters and specifications implemented.

For this project, the qualifications techniques used to qualify the solder print and the solder joints after soldering, were:

- SPI and AOI, to see if there are differences by soldering in an Air atmosphere, and with the presence of "2wt% Ni flux", in some PCBs. With this automatic techniques it's possible to qualify all the PCBs and verify if exists some visual defects;
- Visual inspection, to see the quality of the solder joints, with the help of an optical microscope, and verify if exists visual defects;
- X-ray inspection, to identify visual defects hidden by the components or solder joints. This hidden defects can be for example voids.

All the produced PCBs were verified on SPI and AOI during the process, and at visual inspection were analyzed 32 PCBs (16 of each Reflow condition). Finally were verified at X-ray inspection only 10 PCBs (5 of each Reflow condition).

3.3.1 Line Production Automatic Inspection

Solder Paste Inspection (SPI)

It's very important that the quality of the print solder paste is inspected because approximately 50%-65% of SMT defects are related to the printing process. This inspection after screen-printing is important because the *"prevention of an error is far better than having to correct one"* [55]. So in case of failure the product can be repaired/retest with a reduction of costs and scrap lost [56, 57].

Bosch Car Multimedia utilizes the standard SPI inspection machine, KY-3030VAL Koh Young Technology (figure 26a), to inspect the status of the solder printed surface by examining its height, area, volume and offsets in X and Y. Before the inspection of the PCB's the SPI is configured according to the product in study, and save all the images and respective data [57].

In this project the SPI have the objective of verifying if the solder print follow the Bosch Car Multimedia requirements, and if it was been influenced by factors like more than one Reflow in N_2 or Air atmospheres. Then it will be possible to analyze if the solder has a good adhesion and spreading on the surface.

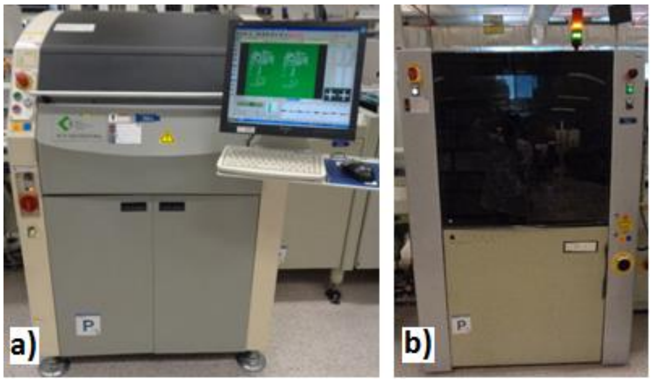


Figure 26. Bosch Car Multimedia Braga automatic inspection equipment's: a) SPI; b) AOI of the Reflow soldering process.

Automatic Optical Inspection (AOI)

As the SPI, the AOI is very important in the quality process of the products because it has the highest precision defects detection and occurs after the soldering process. This is an automatic inspection that is faster, accurate and cheaper than the manual inspection and has got a performance unrivalled in the detection of the smallest of the defects on the PCB [57].

Bosch Car Multimedia utilizes an AOI standard machine, Viscom (figure 26b), to inspect the solder joints, the displacement of each component and to check other possible defects such as missing components, incorrect parts, wrong polarity, bridging and tombstone e.g. As the SPI, the AOI before the inspection of the PCBs is configured according to the product in study, and save all the images and respective data [57, 58].

In this project the AOI has the purpose of verifying if the solder joints follow the Bosch Car Multimedia requirements, and if influenced by factors like the presence of Air inside the oven during the Reflow, e.g.

3.3.2 Visual Inspection

The visual inspection is important to obtain a first characterization of the solder joints quality and to verify the state of the product. It's possible to identify visual defects that weren't detected at the previous inspection equipment's (e.g. AOI) or to analyze some errors detected at the same equipment's. This operation allows to identify defects like non-wetting, bridging, solder oxidation, like others previously described [59].

At the Bosch Car Multimedia production lines the operators utilize a stereo dynascopic microscope, Lynx – Vision Engineering (figure 27a), with a zoom magnification of (7x – 40x) to analyze the "doubt errors" obtained in the AOI.

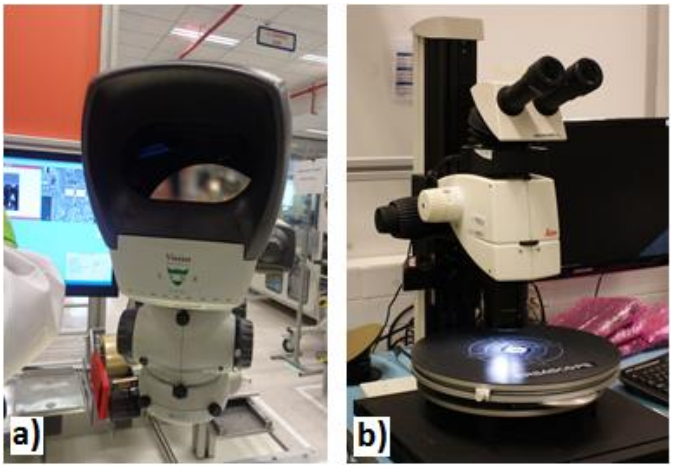


Figure 27. Bosch Car Multimedia Braga visual inspection equipment's: a) Lynx dynascopic microscope; b) Leica M205C optical microscope.

To this dissertation at the MFI2-CP laboratory were utilized an optical microscope, Leica M205C (figure 27b), to analyze the PCB after the Reflow soldering process with a zoom magnification of (7.8x, 25x and 50x). The objective of this visual inspection is doing a first analyze to the solder joints, to see if exists and detect any visual defects like oxidation, lack of solder, like others already described.

3.3.3 X-ray Inspection

The X-ray inspection is an important technique to analyze possible defects that are hidden and not visible to the inspection systems and to the operator. Sometimes these defects are under the component or may be inside the solder joint such as voids, porosity or cracks [59].

This technique consist of applying an x radiation through a sample to produce a shadow image of the internal structure (see example in figure 28a). Depending of the interests of the operator, the X-ray tension and the placement of the sample in the equipment, allows to have better images and magnifications [60].

Bosch Car Multimedia utilizes an X-ray scanner, phoenix x-ray (figure 28b). In this project this technique was important to analyze the possible internal defects of the SMD solder joints, such as voids or porosity. It was also used to verify the quality of the same solder joints. So that, were needed to programming the inspection machine to always analyze the same components/zone of each PCB.

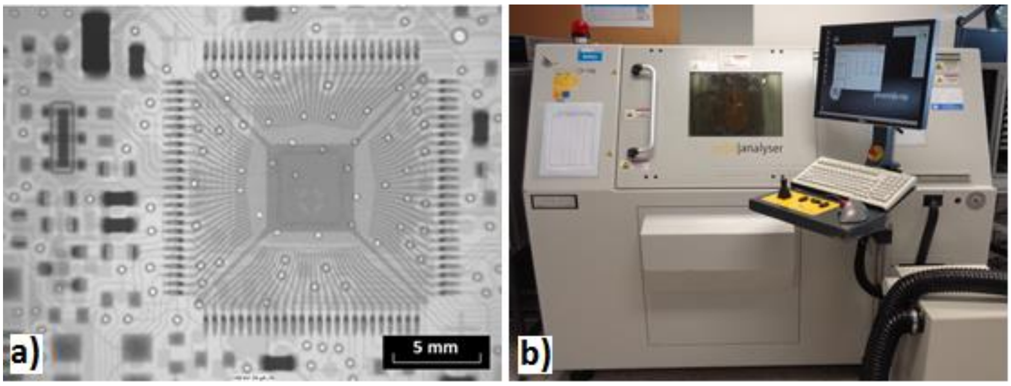


Figure 28. a) X-ray image of part of the SolarA product (after Reflow process); b) Bosch Car Multimedia X-ray scanner inspection equipment.

3.4 Characterization techniques

Most of the research work done at the universities or enterprises include the investigation or production of new materials or products. Then, to qualify and certificate this materials or products it's necessary to use some characterization techniques.

In this dissertation the techniques characterization used have the objective to estimate the performance of the equipment or product during the period of "life" of the material, minimizing the possibility of degradation and undesirable failure during use.

So, to analyze the samples produced/obtained at the university and Bosch Car Multimedia, were used the following techniques:

- Thermal analysis (DTA/DSC), to analyze the melting temperatures of the SAC305 and SAC405 (in N_2 and in Air atmospheres) at the university;
- Optical microscope (OM), to verify the solder joints quality and geometry, and see if exists microstructure defects;
- Scanning electron microscopy (SEM), to measure the thickness and geometry of the intermetallic (with SEM); and to measure the elemental mapping of the samples (with EDS), in particular the samples with Ni added to the flux.

The TGA-DTA equipment, it is also used to soldered samples of SAC305 and SAC405 (with and without "2wt% Ni flux") at different temperatures in an inert and oxidant atmosphere. The samples produced were analyzed at optical microscope and SEM.

The samples produced at Bosch Car Multimedia (SolarA product normal Reflow process and soldering with addition of "2wt% Ni flux" suspension, due to the reduced time and techniques associated costs, only were analyzed 4 samples, 1 PCB soldered with flux plus Ni, and 3 of the removed PCBs after Reflow (these numbers are explained above).

3.4.1 Thermal Analysis

Thermal analysis consists in experimental techniques which allow the study of the materials phase transformation. This is possible by investigating the behavior of a sample as a function of temperature, in a controlled atmosphere. The main techniques of thermal analysis to perform this study are Differential Scanning Calorimetry (DSC), Differential Thermal Analysis (DTA) [61].

Differential Scanning Calorimetry (DSC) is a technique that measures the heat flow, provided separately to the test sample and the reference sample that is necessary to keep them at the same temperature [62].

Differential Thermal Analysis (DTA) is similar to the DSC technique but in this case the test and reference samples are heating, together, with the same heat flow. This technique measures the temperature difference between the test and reference samples [62].

So, with the results of this thermal analysis it is possible to measure the phase transitions of the test sample [62].

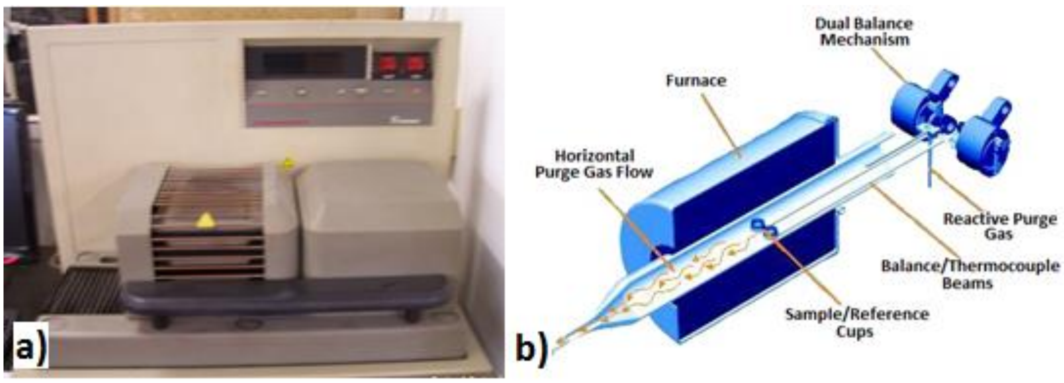


Figure 29. a) University of Minho TGA-DTA equipment, SDT 2960 from TA Instruments; b) DTA-TGA process scheme [adapted from [63]].

At the university metallurgy lab, is used a TGA-DTA equipment, SDT 2960 from TA Instruments (figure 29), to do the thermal analysis.

In this project the objective of using this techniques is to simulate the Reflow soldering process, and measure the melting temperatures of the material in study.

With this technique, first were prepared samples of SAC305, SAC405 to verify fi exists differences on the melting temperatures when soldering in N_2 and in Air atmospheres. Finally were utilized to solder samples of SAC305 with 2wt% Ni flux and SAC405 with 2wt% Ni flux on a PCB substrate coated with Sn.

3.4.2 Optical Microscopy

The optical microscopy it's a test method very used in scientific works like reports and thesis. It allows to do metallographic analysis, study the microstructure of the materials and study the solder joints geometry. Then it's a powerful tool to do microstructural examinations of materials [64].

To analyze the samples produced at the University of Minho and Bosch Car Multimedia, was used an optical microscopy, Keyence VHX-2000 (figure 30) with a zoom magnification of (1000x). The fact of microscope magnify images of small samples allows to study the state of solder quality of the connection between the SMD components and the PCB.

It is possible to analyze small and bigger solder joints and verify if exists microstructure defects, study the solder joints geometry, and is possible to measure the intermetallic phases.

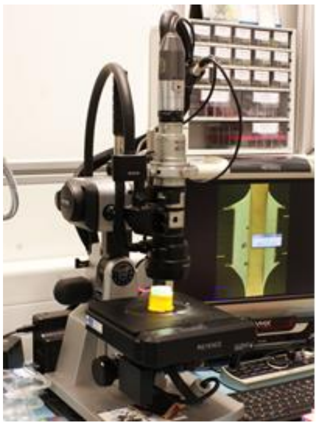


Figure 30. Bosch Car Multimedia optical microscopy, Keyence VHX-2000.

To do a good analyze of the solder joints and their microstructure of a specific zone, it's necessary to cut the sample. First are chosen the zones that wants to study then cut for further analysis. But to obtain an acceptable sectional cut it's necessary to prepare the sample by: preparing the sample surface; mounting with resin, grinding, polishing and finally etching [65].

Samples preparation

In this dissertation are analyzed at Bosch Car Multimedia optical microscope, the samples produced at the University of Minho and the cuts effectuated to the product obtained at Bosch Car Multimedia. But the University samples had a slightly different preparation comparing to the other samples, relatively to the grinding and polishing step.

➢ Procedure performed at the university:

- Grind a bit of sample surface with an abrasive paper (e.g. 180 mesh) to facilitate the mounting resin;
- Put the sample inside a mold with the grinding surface turned down, then add resin (mix of two parts of powder, with one part liquid). Wait 8 hours for the resin solidification;
- Grind the mounted samples (figure 31a) with the abrasive papers of 180, 600 and 1200 mesh, with Mecapol 260 equipment (figure 31b);

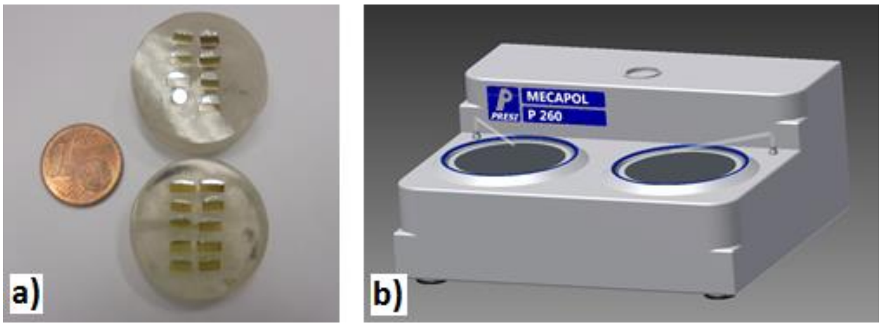


Figure 31. a) Mounted samples from university and b) Mecapol 260, used at University of Minho in (Inventor drawing).

- Polish with a nylon cloth of 6 μm and 1 μm with diamond abrasive;
- Etching to reveal the microstructure of the surface with a solution of (5 g of Ferric Chloride + 2 ml of Hydrochloric acid + 96 ml of Ethyl alcohol).

➢ Procedure performed at Bosch (Marques Ferreira chemical lab):

- Cut a sample at the analyzing zone with a cutting disk, then grinding a little bit the surface to facilitate the mounting resin;
- Put the sample inside a mold with the grinding surface turned down, then add resin (mix of two parts of powder, with one part liquid). Wait 8 hours for the resin solidification;
- Grind the mounted samples (figure 32a) with the abrasive papers of 320, 500, 800, 1200, 2500 and 4000 mesh, with a Struers RotoPol-21 equipment (figure 32b);

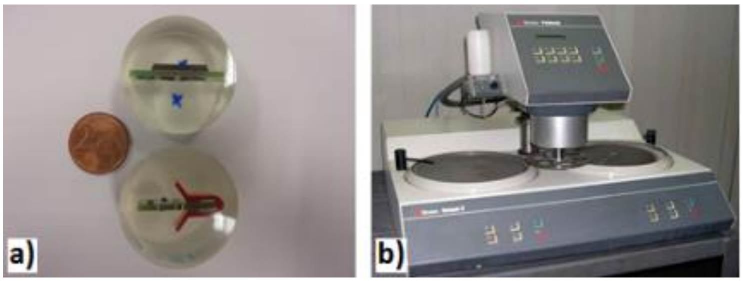


Figure 32. a) Mounted samples from SolarA product cuts and b) Polishing machine Struers RotoPol-21 [adapted from [66], used at Marques Ferreira chemical lab.

- Polish with a nylon cloth of 3 µm and 1 µm;
- Realize two etchings to reveal the tin (93ml of distilled water + 5ml of Nitric acid + 2ml of Hydrochloric acid), and other to reveal the copper (20ml of Ammonia + 20 drops of hydrogen peroxide at 20% volume).

This procedures are important to get good images under the microscope and future analysis as SEM. The last step is essential to analyze the intermetallic layer.

Sectional cuts

For the characterization of the SolarA Bosch product at optical microscope and SEM/EDS, were chosen three different components. The choice was made according the criticalness of each component, then were selected a QFP, one resistance and one capacitor.

To minimize the number of sectional cuts (because of the price of every one), were selected one resistor and a capacitor close to one other (at the same cut plane) (figure 33). Were cut 3 SolarA PCBs, and 1 SolarA PCBs with an application of "2wt% Ni flux", for each condition (soldered in a reflow process in N_2 and in Air atmospheres).

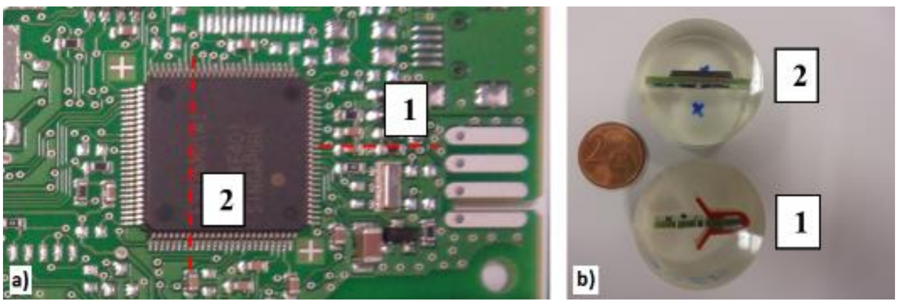


Figure 33. a) Areas of sectional cuts: 1- resistor and capacitor; 2- QFP; b) Samples resulting from the cuts.

The study of the solder joints geometry, elemental mapping and intermetallic thickness, were analyzed by SEM-EDS.

3.4.3 Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS)

The scanning electron microscopy (SEM) technique is one of the most versatile equipment for the analysis of the microstructure morphology and chemical composition characterizations. This technique uses a focused electron probe to extract structural and chemical information from specific regions of a sample [67].

This is a non-destructive technique that consists in exciting the atoms of the sample surface with an incidence of an electron beam. This excitation causes a release of energy by the electrons in the range of X-ray, which allows to do an identification and quantification of each elements present in the sample. This is possible because the energy released, depends on the atomic structure of each element present [67].

To study the samples obtained at the university and at the enterprise was utilized a SEM/EDS equipment from Bosch Car Multimedia of Braga, Hitachi TM3030Plus (figure 34).

Figure 34. Bosch Car Multimedia scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy (EDS), Hitachi TM3030Plus.

This technique is a powerful tool for this dissertation in order to evaluate the chemical constitution and the elemental mapping (presence and distribution of adding Ni) by EDS, and measure the thickness and geometry of the intermetallic by SEM.

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter are presented and discussed the results obtained in this dissertation.

First are presented and analyzed the results obtained at Bosch Car Multimedia production line (Reflow soldering), namely of the SPI, AOI, Visual inspection and X-Ray tests, and the cuts performed on three components types of different PCBs. These results allow to evaluate the difference of soldering in an inert atmosphere (Nitrogen) and in Air and to detect the presence of possible defects. In each of these analyzes, in order to verify if there is improvement in the results, a comparison is made between normal PCBs processed and PCBs with Nickel particles added.

Secondly, and with the same purpose of improving the results, are presented the results obtained from the laboratorial tests, at the University of Minho. Initially are presented the melting temperatures results of the two solders used and tested in different atmospheres, then the results from the addition of Nickel particles into the solder flux. For the addition of Nickel tests, the influence of soldering in different atmospheres (with Argon and Air) and the soldering with different temperatures, are analyzed. For all of these results are studied the solder joints geometry, chemical constitution and elemental mapping, and the intermetallic thickness.

4.1 Bosch - Solder Paste Inspection (SPI)

According to the Bosch standards, the main objective of the SPI is to verify if there is a good solder paste printing, for the tested conditions. This way are analyzed the SPI data obtained of the most critical component present in this product (QFP component). This component is the most critical because of the high number of pads with a reduced area where the solder has to be printed on the PCB.

In figure 35 are presented the results obtained from the SPI analysis to all boards in the QFP zone, related to height, area and volume of printed solder paste. This analyze includes all the 328 PCBs to be soldered in an atmosphere of N_2 and Air, including the PCBs with “2wt% Ni flux”.

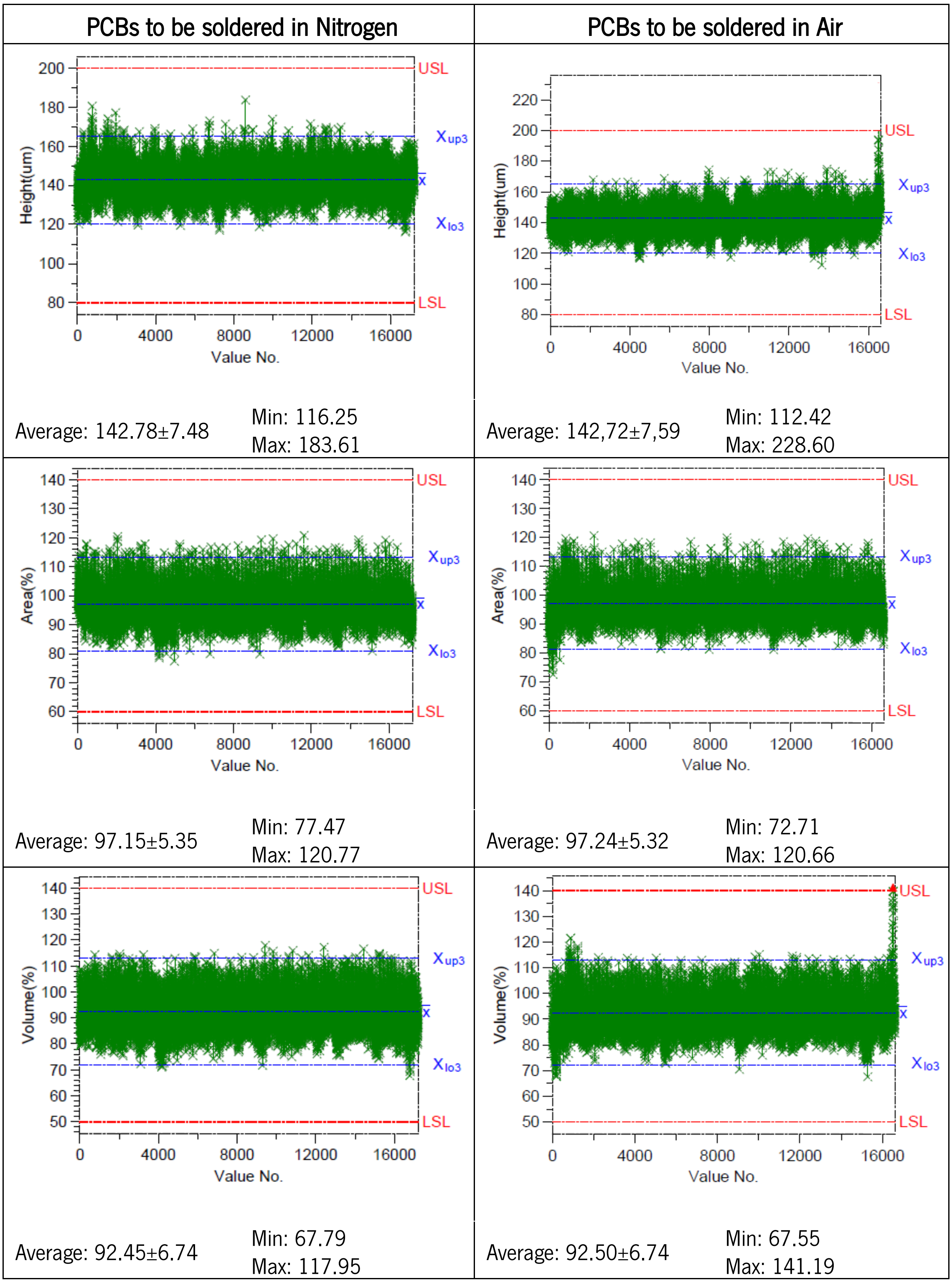


Figure 35. Results from the solder paste printing of all PCBs – QFP component.

At the figure 35 are represented the height, area and volume values as function of total number of pads printed of all analyzed PCBs, of the QFP component (Value No. axis).

After analysis of the SPI results, it is possible to verify that there are no differences in height, area and volume of the printed solder paste between the tests with inert atmosphere and in Air. There were no problems on solder paste adhesion and spreading, and the values meet the Bosch requirements.

Simultaneously, it can be concluded that the presence of flux with 2wt% of Ni particles, on the surface of 12 PCBs, does not influenced the SPI results.

4.2 Bosch - Automatic Optical Inspection (AOI)

The main objective of the AOI is to analyze each PCB at the end of the Reflow line, and to verify the existence of error or pseudo-errors, alerting the line operator if necessary. Most of the times the AOI inspection detects the presence, not of errors, but of pseudo-errors. These pseudo-errors are a process indicator, and arise when the AOI software does not know if the detected anomaly is or is not an error, then it alerts the operator. Then the operator should make a visual analyze of the PCB to confirm the presence or absence of an error.

The AOI data analyzed was obtained from the normal production of the SolarA product, in N_2 and in Air atmospheres, and the data obtained from this product product with "2wt% Ni flux" added.

In table 6 and figure 36 are presented the results obtained from the AOI analysis of the 316 PCBs soldered in an atmosphere of Nitrogen and Air, and the 12 PCBs with "2wt% Ni flux" soldered in the same conditions.

Table 6. Number of PCBs analyzed and the total of errors and pseudo-errors detected, for each condition.

	SolarA PCBs	Total Errors	Total of pseudo-errors	SolarA with "2wt% Ni flux"	Total errors	Total of pseudo-errors
N_2 atmos.	158	0	300	6 (+5%)	0	12
Air atmos.	158	0	956 (+318%)	6	0	*

*not accounted due to the lack of components in the insertion feeder.

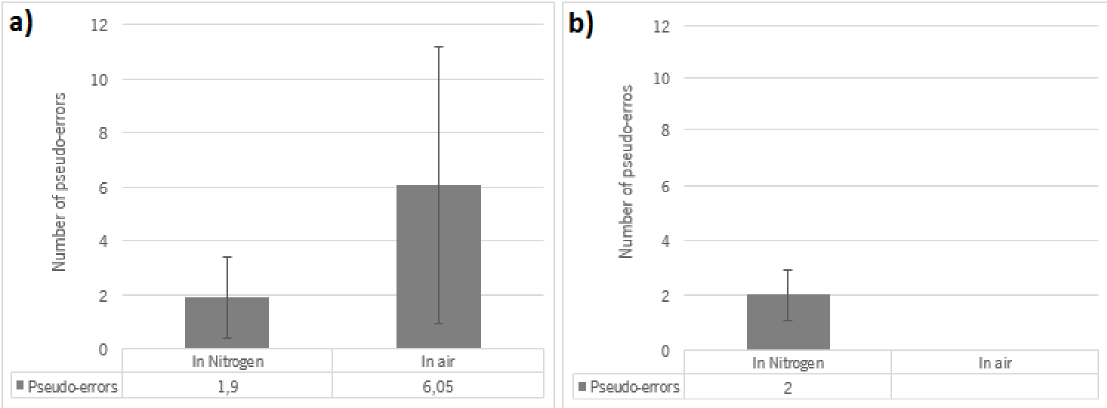


Figure 36. Average of errors detected by the AOI per PCB: a) SolarA normal PCBs; b) SolarA PCBs with "2wt% Ni flux".

After analysis of all the AOI results, it is possible to verify that no errors are detected during the Reflow soldering process in N_2 and in Air atmospheres. Only pseudo-errors were detected, that where not confirmed as errors by the line operator. Comparing the results obtained in the Reflow, in N_2 and in Air atmosphere, it is possible to verify that, in Air the number of pseudo-errors tripled (increasing about 318%). This may be because soldering in Air can affect the brightness of the solder, and because a no-clean flux (PCB without washing after Reflow), as used. The flux may present a brown or yellow coloration after soldering [42]. Then, as the AOI works with images with brightness and a gray scale, slight variations of color and brightness in these obtained images, the inspection system (AOI) consider them as pseudo-errors.

All PCBs with pseudo-errors detected were inspected by the line operator, and with the aid of a defect catalog, determined the existence of errors. It is concluded that all the boards were approved without defects.

The boards with "2wt% Ni flux" soldered in the Air atmosphere, the pseudo-errors were not considered, due to the lack of components in the insertion feeders. However, analyzing the results obtained of the boards with "2wt% Ni flux" soldered in the atmosphere of Nitrogen, it is verified that placement of Ni particles at the beginning of the process, does not influence the results of the AOI, obtaining the same average of pseudo-errors per plate (about 2/PCB) increasing only about 5% comparing to the PCBs without Ni.

4.3 Bosch - Visual Inspection

The main purpose of the visual inspection is to analyze the PCBs in which were detected pseudo-errors in the AOI inspection. Through an enlarged image with an optical microscope, it is possible to analyze all the surface of the PCBs, as the appearance and quality of the solder joints and check for defects. In detail were analyzed, 16 PCBs of each condition (Reflow in N_2 and in Air atmospheres).

Due to the similarity of the results, in figure 37 are presented only some obtained images of three components under study, QFP, capacitor and resistor, soldered in different Reflow atmospheres, in N_2 and Air.

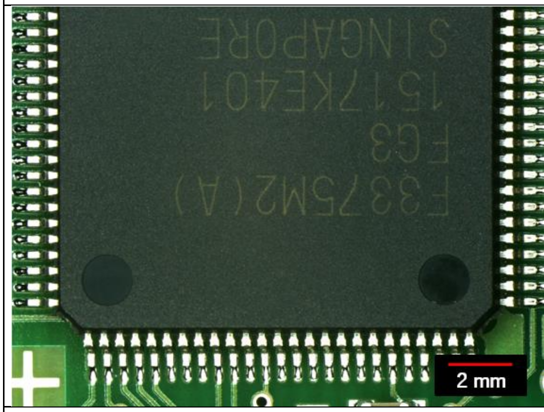
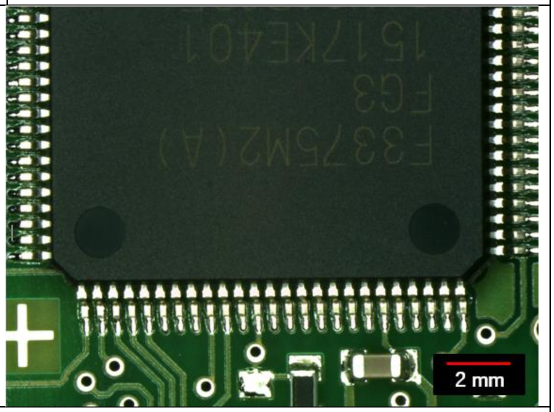
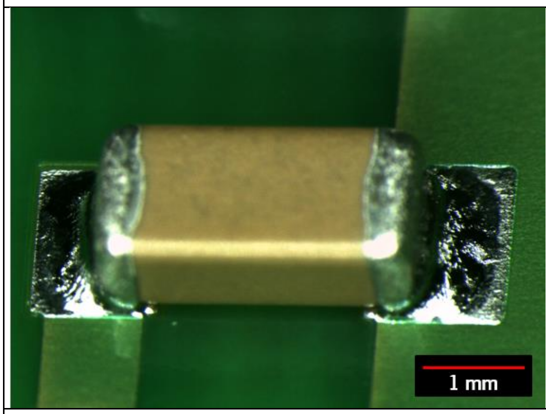
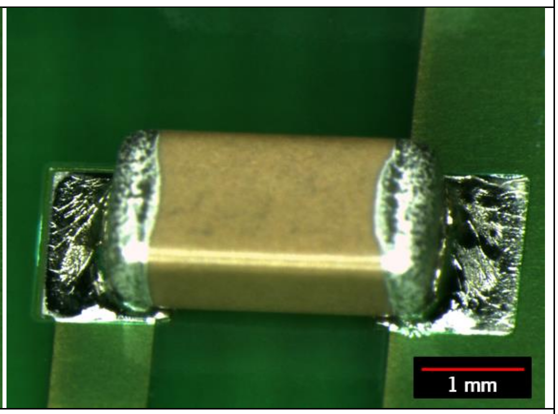
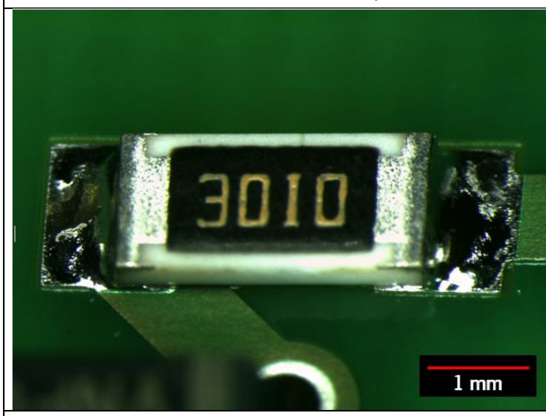
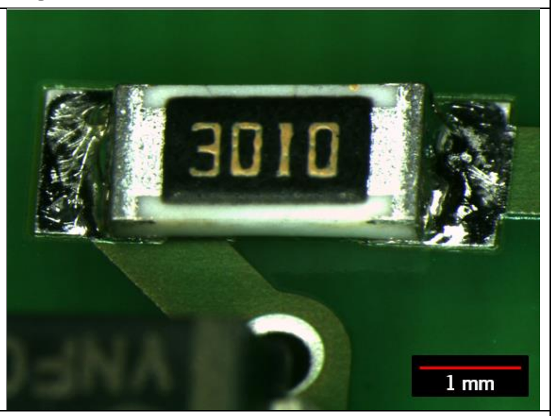
PCBs soldered in Nitrogen	**PCBs soldered in Air**
PCB code number: 4201	PCB code number: 4308
	
QFP - zoom magnification (7,8x)	
	
Capacitor - zoom magnification (25x)	
	
Resistor - zoom magnification (25x)	

Figure 37. Images obtained by visual inspection of three PCA components (chosen randomly) soldered in N_2 and in Air atmospheres.

After analyzing the PCBs surfaces with the optical microscope, and according to the images obtained above it is possible to verify that there are no significant differences in the PCB surface appearance and on the solder joints.

All the solder joints appear to be well soldered, without any defect (black zones that appear in the solder joints are shadows related with the position angle of the PCB during the analysis).

By visual inspection performed to the PCBs with “2wt% Ni flux” soldered in different atmospheres, and comparing to the normal PCBs soldered, the results are the same (no defects detected). However, it may be concluded that for the process conditions used, soldering in Air atmosphere, has no visual interference.

4.4 Bosch - X-ray Inspection

The main objective of the X-ray inspection is to verify the existence of defects under the components (in soldered hidden zones) that cannot be observed in the AOI and visual inspection. Thus, with X-ray it is possible to evaluate the presence of voids in the solder joints.

For this test the components to the analyzed should be the most critical in terms of presence voids, for this purpose was selected the SOT component (the only present in the PCB). This is the component selected because it is a Bottom Termination Component (BTC). BTCs are components which have metalized terminations or pads underneath the package, so they are susceptible to have voids in the soldered joints [68].

In figure 38 is shown an example of the obtained images in the X-ray inspection to PCBs soldered in Reflow with N_2 and Air atmospheres.

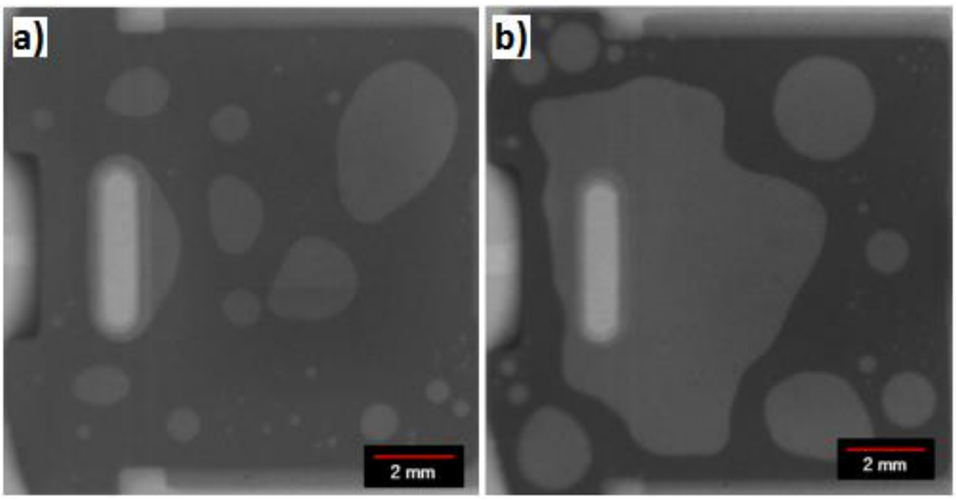


Figure 38. Images obtained of the X-ray inspection to the SOT component soldered in Nitrogen (a) and in Air (b) atmospheres.

Then using the image analysis software ImageJ, it was possible to quantify the percentage of voids to the 10 PCBs analyzed in the X-ray, soldered in different atmospheres. The results obtained are shown on the following figure.

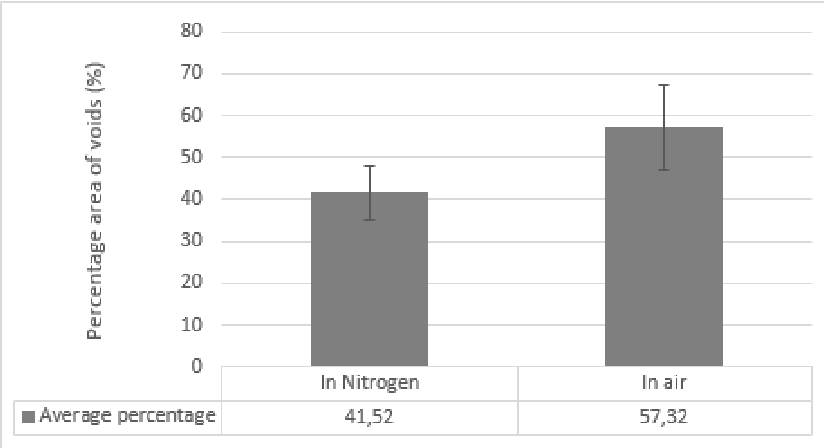


Figure 39. Average of percentage area of voids detected in the X-ray inspection, for the 10 PCBs analyzed, soldered in different atmospheres.

After analyzing the X-ray images of the SOT component, it is possible to verify a significant amount of voids in the solder joints. It is normal to have voids in the solder joint even when soldering with an inert atmosphere. This normally happens because of the entrapped outgassing during the flux reaction with the metallization of the substrate and component and, also, from the evaporation of the solvent in the solder paste during the Reflow process [69, 70].

The SOT component soldered in an Air atmosphere presents a higher percentage area of voids. This may happen because of the presence of a higher solder surface oxidation causing outgassing flux and gases to be entrapped in the solder joint. The fluidity of the melted solder may decreases, hindering the exit of gases to the exterior of the solder joint and increasing the percentage area of voids [70].

4.5 Bosch – Samples Cut

To study the solder joint geometry, constitution and intermetallic compounds characteristics, were prepared samples of the normal SolarA PCBs and SolarA PCBs soldered with “2wt% Ni flux” added. Then were selected and cut three components: one QFP, one Capacitor and one resistor of the PCBs. After polishing they were analyzed with the optical microscope and SEM.

In figure 40 is shown an example of the optical microscope images obtained from the cuts made, to the three components in study.

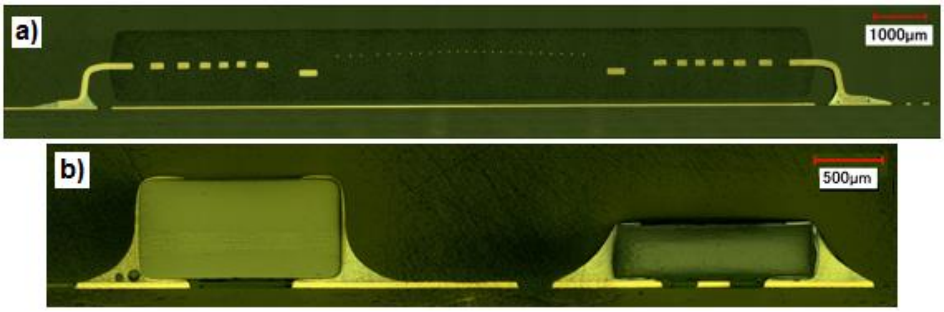


Figure 40. Optical microscope images obtained from the cuts made on a QFP (a) a Capacitor (b) (left) and a Resistor (right) (c).

From these samples cuts, made on the PCB produced in a N_2 and in Air atmospheres, was studied the solder joint geometry, the solder chemical constitution and the intermetallic layers.

4.5.1 Solder Joint Geometry

The solder joint geometry is one of the keys to have a reliable bonding of the components on the PCB. Thus, the solder joints must satisfy some requisites in terms of the geometry and height of the meniscus formed, and the distance between the board pad and the components lead (pin).

In figure 41 is shown the local where the height measurement was made, and on table 7 are presented the average values of the heights measured to the left pin of the QFP component, of some PCBs produced with different conditions. The heights of the other pin are not presented due to its similarity.

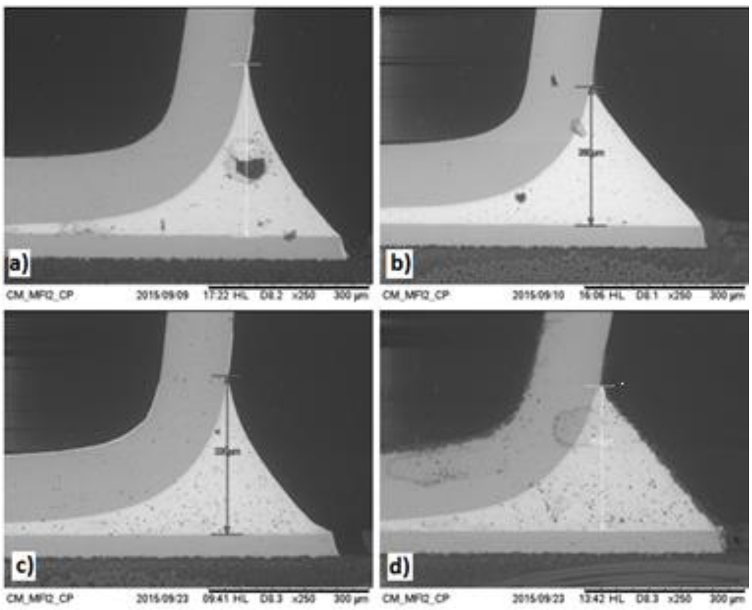


Figure 41. SEM example images of the local where the heights was measured from the: QFP soldered in Nitrogen (a) and in Air (b); QFP soldered on the PCB with "2wt% Ni flux" soldered in Nitrogen (c) and in Air (d).

Table 7. Average values of the heights of the left pin of the QFPs measured.

	Solder joint height (μm)	
	Soldered in Nitrogen	Soldered in Air
SolarA	326.33±13.05	252.3±10.02 (-22.7%)
SolarA with "2wt% Ni flux"	320	290 (-9%)

The solder joints heights were measured to three QFP component's leads of the PCBs soldered without Ni, and one of the PCBs soldered with "2wt% Ni flux". Then, according to the values obtained it is possible to verify that the PCBs soldered in the Reflow soldering process under an atmosphere of Nitrogen, present higher heights comparing to those soldered in Air (about 22.7% smaller). It is also possible to verify, that soldering with Nitrogen promotes a concave solder fillet in shape [53], resulting from the good wetting of the solder to the parts being joined. This happens because when soldering in an inert atmosphere, oxides are not (or less) formed and so the solder wets better the surface pad and the pin of the QFP (lower contact angle).

Soldering in Air promotes the existence or superficial oxides, which are more difficult to remove, especially in the pins or leads of the components, due to the flux not reaching the entire contact area to solder. Therefore, the wetting decreases, the contact angle increases, and the solder fillet is not concave.

The difference between the heights measured is not associated with the quantities of printed solder, because as already seen at the SPI results (sub chapter 4.1), there is no differences in the height, area and volume results.

The fact of adding Nickel particles on the PCB surface, does not present significant changes in the height of the solder joint and its geometry, comparing to the results of the PCBs without Ni. As verified from the results obtained, the Ni particles may not influence the height and geometry of the solder joint, because these particles were added on the surface of the PCB's pad, and not on the component's pins. However more measures should have been made to obtain a better conclusion.

At the appendix I are presented similar images as the QFP for the other components: Capacitor and Resistor. The results obtained from the height measure and solder geometry, present the same tendency.

Now looking at the figure bellow, it is possible to see the influence of soldering in N_2 or in Air atmospheres. Thus, in figure 42 are shown some images obtained from the optical microscope (chosen randomly) that shows the complete solder joints formed in the pins (leads) of each component in study.

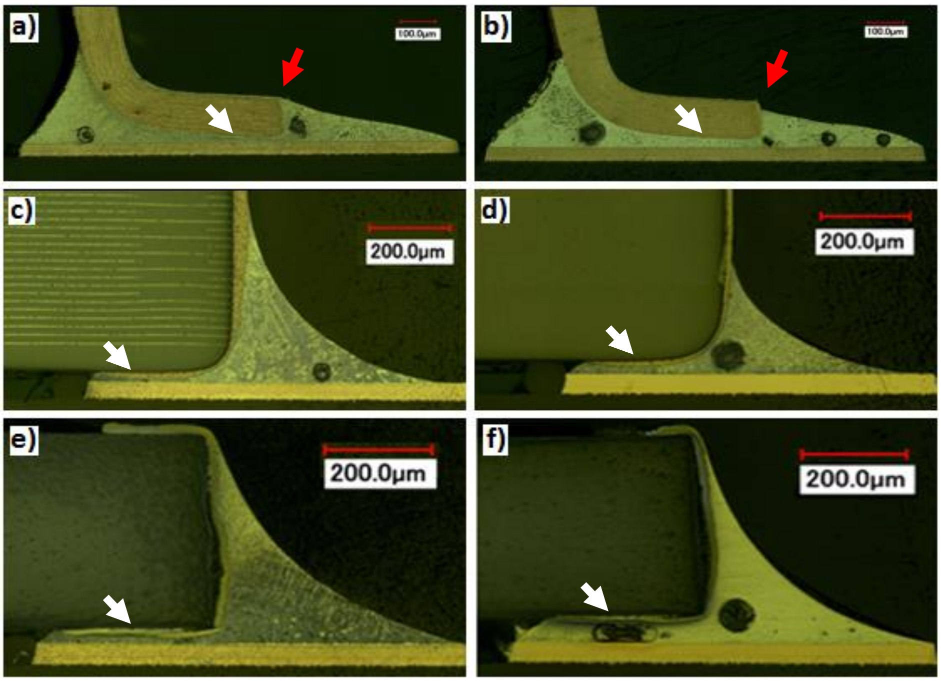


Figure 42. Optical microscope images of the solder joint geometry from the components soldered on normal board: soldered in Nitrogen, QFP (a), Capacitor (c) and Resistor (e); and soldered in Air QFP (b), Capacitor (d) and Resistor (f).

From the figure above, as already verified, the solder joint height is higher when an inert atmosphere in the Reflow soldering process is used. To show that soldering in an Air atmosphere influences the wetting of surfaces to join, the QFP pin zone signalized with a red arrow can prove it. Because, if is possible to see that the solder does not reach the top surface of the QFP pin, comparing to the QFP pin soldered with Nitrogen. As already explained above, this may happen because of the existence of formed oxides on the surfaces of the pin during the soldering process. Thus, as the flux does not reach the top surface of the pin, oxides can be formed, so the solder does not wet and solder that area.

It is also possible to verify the existence of voids in the solder joint, and in a qualitative analysis it is possible to say that Reflow soldering in Air may increase the number of voids. This phenomenon is also visible in the remaining images obtained.

According to figure 43, although the more aggressive chemical attack, it is possible to verify the QFP component's lead soldered with "2wt% Ni flux" added, present similar results as the presented above, for each atmosphere studied. The zone signalized with a red arrow presents the same behavior, and is expected that Ni does not influence here because these particles were added on the PCBs surface instead of the component's lead surface. To the PCBs soldered with "2wt%

Ni flux" the solder spreads all over the pad independent of the atmosphere, but the solder joint height is less when soldering in Air, as already seen.

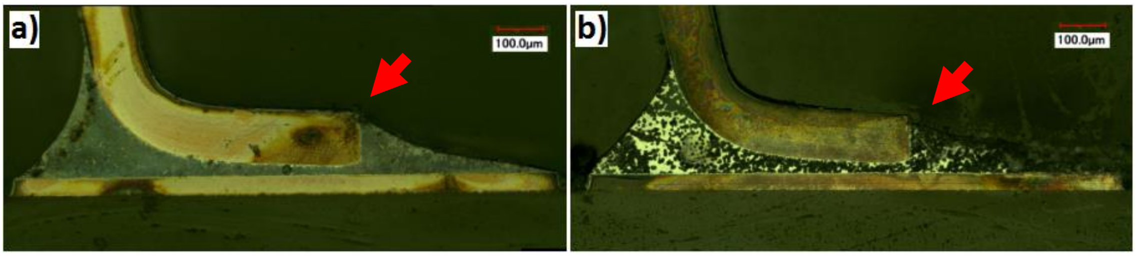


Figure 43. Optical microscope images of the solder joint geometry of the QFP component soldered in N2 (a) and in Air (b).

Comparing the solder joints obtained in the different soldering conditions with the IPC-A-610 requirements (figure 44), the solder fillets height and geometry allows to accept all the PCBs produced.

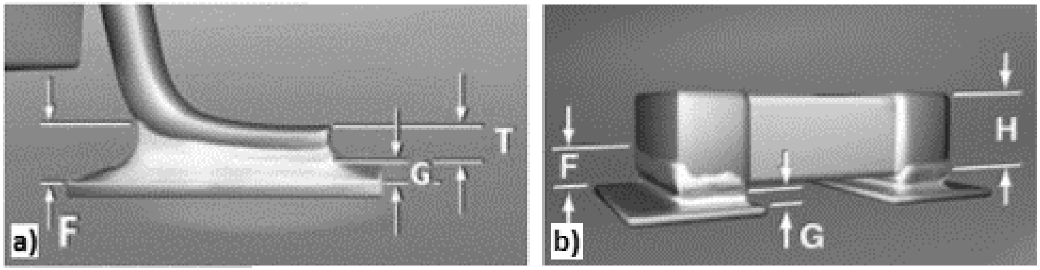


Figure 44. IPC-A-610D acceptance criteria of Class 3 for the SMD solder fillet [adapted from [53]].

In figure 42 the zone signalized with a white arrow correspond to the solder thickness between the pin and the pad of the PCB (G). According to the class 3 of the IPC-A-610D (8.2.5.6), to the QFPs pin, the solder joint is accepted if the fillet height (F) is equal or greater than solder thickness (G) plus lead Thickness (T). According to the class 3 of the IPC-A-610D (8.2.2.6), to the Capacitor/Resistor lead, the solder joint is accepted if the fillet height (F) is equal or greater than solder thickness (G) plus 25% termination height (H) or 0.5 mm [53]. Therefore all the solder joints analyzed satisfy these requisites so the product can be accepted.

4.5.2 Solder Joint Chemical Constitution and Elemental Mapping

From the SEM-EDS images obtained of the solder joints, of the three components in study, were made an elemental mapping to know the elements distribution in the solder and in the component pins (leads).

Normal SolarA PCBs

In figure 45 are presented the mappings obtained from the solder joint of the left pin of the QFP, soldered on a normal PCB in a Nitrogen atmosphere, where it is possible to analyze the constitution of the solder joint.

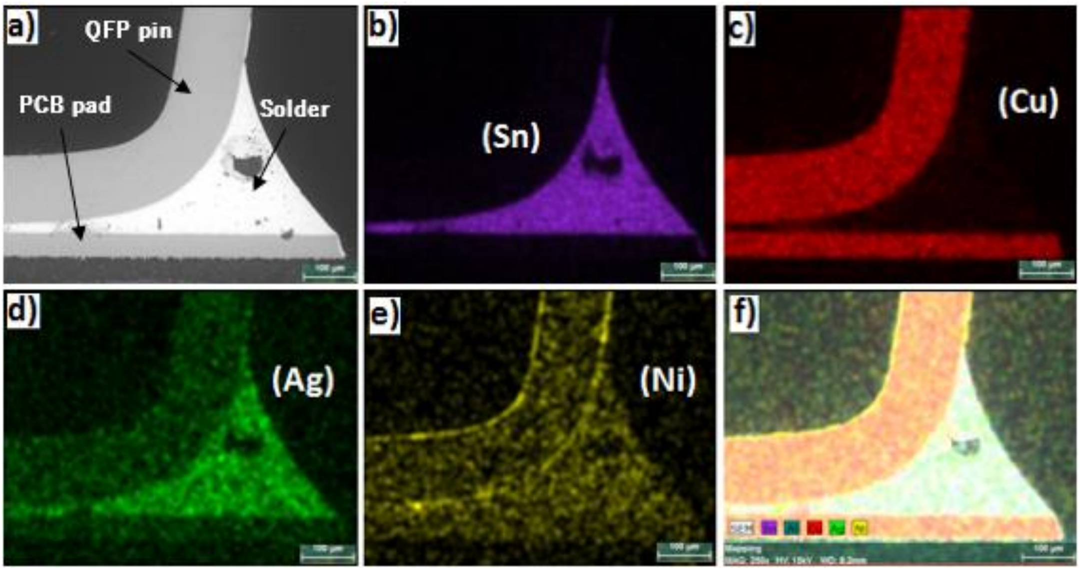


Figure 45. Images of the solder joint formed at the QFP left pin, soldered on a normal PCB in a Nitrogen atmosphere (a) and corresponding elemental maps Sn (b), Cu (c), Ni (e), Ag (f), and all maps combined (f), in a scale of 100 µm.

With the mapping results presented above, it is possible to analyze the constitution of the solder, PCB pad and the component's pin. From the results of the elemental maps it is possible to verify that the solder has mainly Sn (at purple), than has Ag (at green) and finally it is possible to see a reduced presence of Cu (at red). The results obtained are correct because the solder in use is SAC405 (Sn-Ag-Cu).

According to the PCB pad and component pin, it is possible to see a high concentration of Cu (at red), and this is true because the pads of the PCBs and pins (leads) of the components used, are made of Cu. It is also possible to see the presence of a small layer of Ni surrounding the components pin. This presence of Ni shows that the components pin have a metallization of Ni. The mapping obtained for the Capacitor and Resistor, presented in appendix II, soldered in Nitrogen on the normal PCBs, present the same results. The mappings obtained from the components soldered in Air atmosphere presents the same results that the components soldered in Nitrogen.

Finally it should be noted that the Ag and Ni elemental maps present interferences due to their small quantity existent. The fact of detecting Ni in the solder and Ag in the component's pin can be explained by the occurrence of some errors during the SEM analysis, due to their small presence in the sample.

The Aluminum detected as shown in all the combined maps, is resulting from the lubricant used in the polish samples, which contains particles of Alumina. In the case of the Resistor (appendix II), the larger concentration of Aluminum corresponds to the component constitution.

SolarA PCBs with "2wt% Ni flux"

Images of the solder joints mapping, with Nickel particles added to the PCBs surface, were analyzed before the soldering process.

From the analyze of images obtained from the three components studied, soldered in N_2 and in Air atmospheres, were always found Nickel particles in the interface of the PCB pad with the solder. Some SEM-EDS images that shows the existence of the Nickel particles in the solder joint, after the Reflow soldering process, are presented in Figure 46.

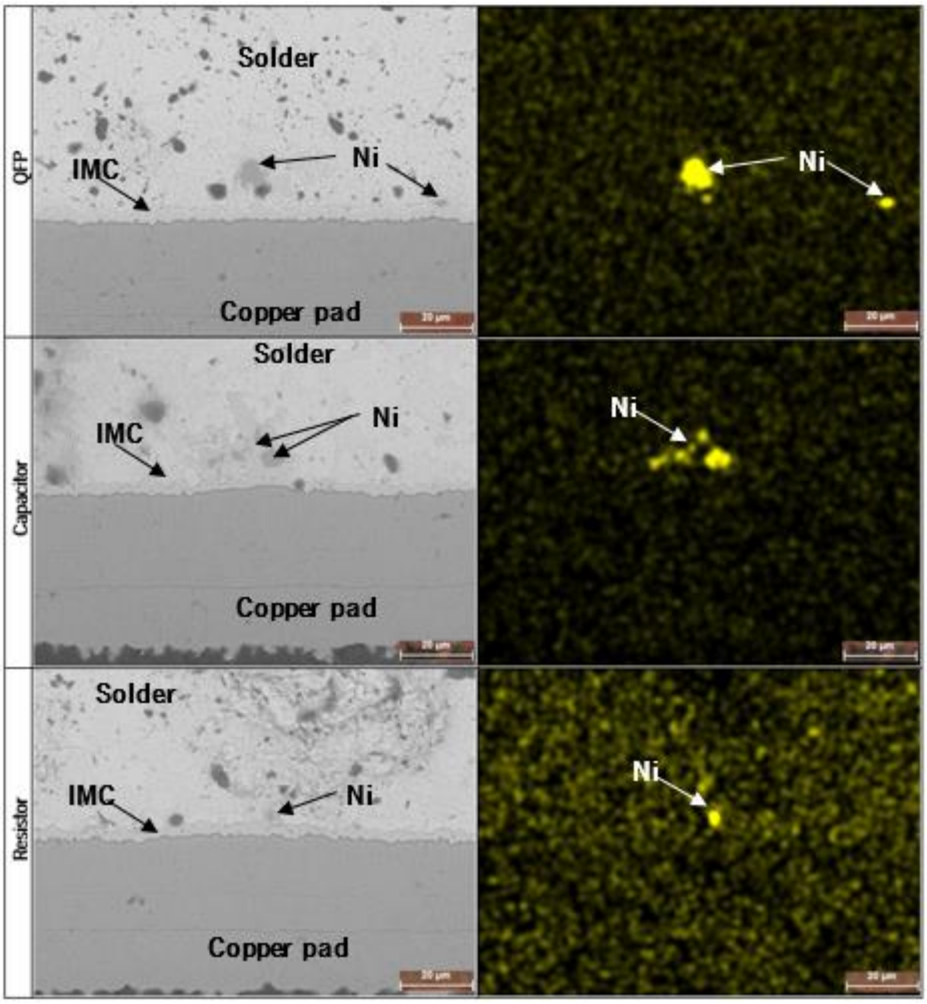


Figure 46. SEM-EDS elemental mapping of the QFP, Capacitor and Resistor left pin (lead), soldered on the board with "2wt% Ni flux" in a Nitrogen atmosphere (scale of 30 μm).

First of all, from the mapping performed to the boards soldered with Nickel particles added on surface, it is possible to verify that these particles are inside of the intermetallic layer. In the rest of the solder joint were not found Nickel particles. It is possible to verify that the intermetallic grows around the Ni particles with a strange morphology. According to the literature [38], it is possible that during the Reflow process a Cu-Ni-Sn IMC can be formed due to the possible reaction of the Ni particles with the solder and the initial Cu-Sn IMC type formed. The intermetallic above the Ni particles, has a kind of sunflower morphology [37, 40].

To understand better the results of the possible Nickel reaction with the Cu-Sn IMC and solder, after the Reflow, in figure 47 is compared the results obtained in this dissertation, with some identical results from the literature. In this paper Ni particles were added into a Sn-3.5Ag solder paste and was subjected to a Reflow soldering process (used maximum temperature of 280°C) [38].

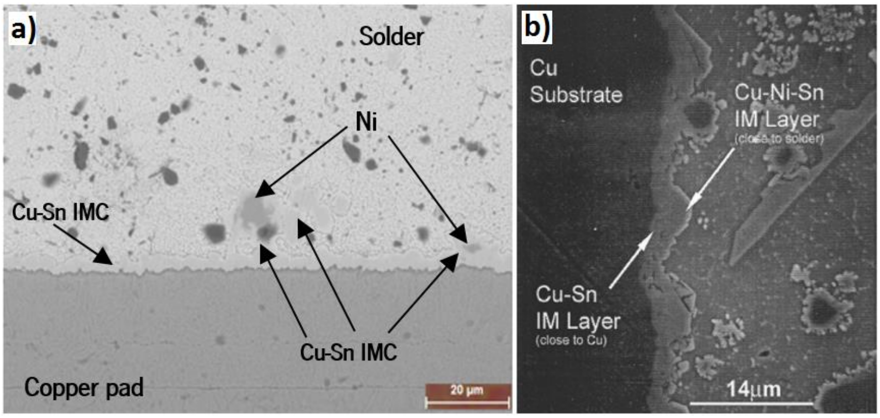


Figure 47. Results obtained from the reactions of Nickel in the solder during the Reflow soldering: a) example of the results obtained in this dissertation; b) results obtained from a scientific paper [adapted from [38]].

According to the results of the scientific paper found in literature, it is possible that the Ni particles added in the flux, react with the solder during the Reflow, and apart from the intermetallic formed by the reaction of the solder with the Cu pad (Cu_6Sn_5 and Cu_3Sn), may be formed another intermetallic (Cu-Ni-Sn).

To finalize, according to the presence of Ni in the solder joint after the Reflow soldering process, it is possible to say that adding Ni particles through the flux by pulverization, proves to be effective, because it is possible to find Ni in the samples. Cannot be conclude much more about addition of Ni particles with flux on the PCBs, soldered in N_2 and in Air atmospheres, because the results are similar. The results of soldering in Air are presented in the appendix III.

As Bosch utilizes internal acceptance criteria and procedures for their productions, for better conclusions about adding Ni particles on the PCB before the soldering process, some detailed tests will be made at the University.

4.5.3 Intermetallic Layer

The intermetallic layer formation is fundamental to ensure the bonding between the solder and the components. The thickness of the IMCs need to be controlled because its brittleness can cause some concerns with the solder joint. Thus, as the IMC are affected by time and temperature used in the Reflow process, the soldering parameters used, need to ensure the formation of an intermetallic layer with a controlled thickness [71].

In figure 48 are shown some optical microscope images obtained of some examples of the intermetallic layer obtained on the PCBs Reflowed with and without Ni particles added, in an atmosphere of N_2 and Air.

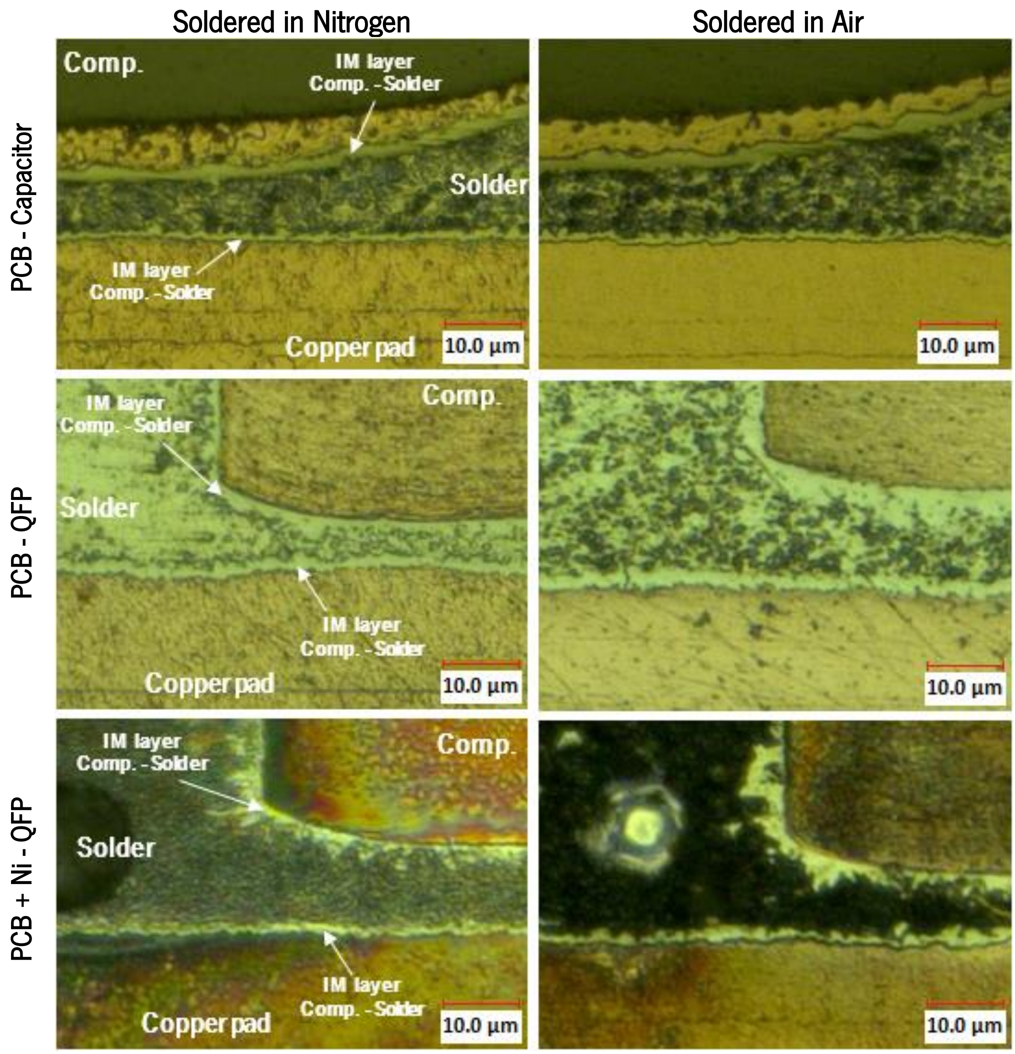


Figure 48. Optical microscope images of some examples of the intermetallic layer after Reflowing in N_2 and in Air atmospheres.

Analyzing all the images of the bonding areas of the PCBs and components soldered, it is possible to verify the formation of an intermetallic layer in all of them. This shows that solder joints promotes mechanical and electric connection of the PCB pads with the components pins (leads). It is also possible to verify that the intermetallic morphology is similar in the different components soldered, including in the PCBs with Ni particles added on the surface.

The images of the PCB soldered with Ni particles show a darker solder, this is explained by the fact of the chemical attack was more aggressive.

Then, in figure 49 are presented the average thickness values of the intermetallic layer measured on some soldered PCBs. In this image is also represented the zones where each component was measured.

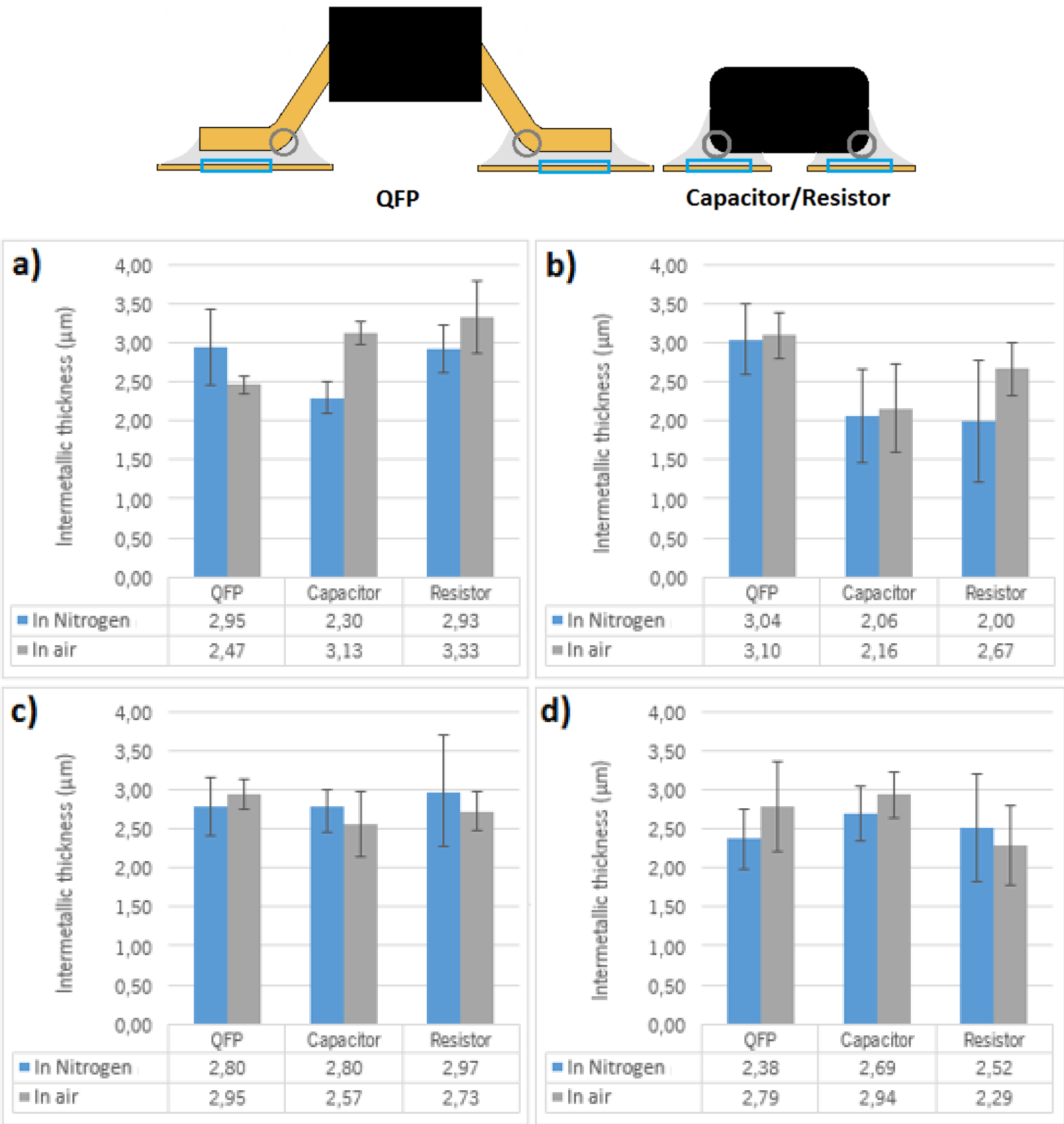


Figure 49. Intermetallic thickness average values measured in different atmospheres to the: a) IMC pad-solder b) IMC solder-component; c) IMC pad-solder (PCBs with Ni); d) IMC solder-component (PCBs with Ni).

According to the results obtained and taking into account possible errors of the thickness measuring, there is only a slight difference in the values obtained. The differences between the thicknesses measured and according to the standard deviation, are related with the fact that the intermetallic formed is irregular, and may be related with the tolerances of the process, parameters and materials used.

This way it is possible to say that the fact of using an atmosphere of N_2 or Air may not influence the formation and thickness of the intermetallics pad-solder and solder-component formation. It is possible to say that both intermetallic, pad-solder and solder-component, grows at the same time with the same formation rate. The same conclusion can be taken from the results obtained from the PCBs soldered with Ni particles added, because comparing the pad-solder intermetallic thickness measured, the results are identical.

Finally, it is possible to verify that the intermetallic thickness values are about 3 μm of thickness, and this value is in agreement with the Bosch internal acceptance criteria and procedures.

4.5.4 Ni Particles Morphology and Size

In order to better understand the Ni particles adding on the PCB surface was deposited Ni particles on the SEM-EDS substrate with the same used technique, pulverization. With this it is possible to have an idea of the distribution that the Ni particles have on the PCB surface, and know their average diameter.

Figure 50 presents the SEM images obtained, in which it is possible to see the distribution and average diameter of the 2wt% Ni particles introduced with flux, pulverized on the substrate surface.

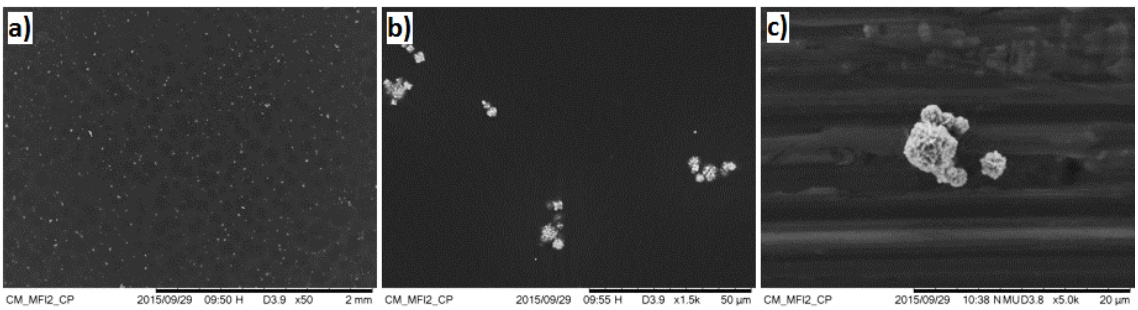


Figure 50. SEM images resulting from the pulverization of the "2wt% Ni Flux" on the substrate surface, representing the distribution in different scales a) 2 mm, b) 50 μm and c) 20 μm.

Analyzing the SEM images it is possible to see that the Ni particles are homogeneously distributed over the substrate surface area, but highly disperse. This means that the percentage of Ni particles addition should be optimized to obtain a mean particle distribution in accordance with the pad size and distance. It is also possible to verify the existence of agglomerated particles.

Figure 51 presents a histogram of the Ni particles size distribution (above analyzed) and table 8 presents their average size, of 30 measurements.

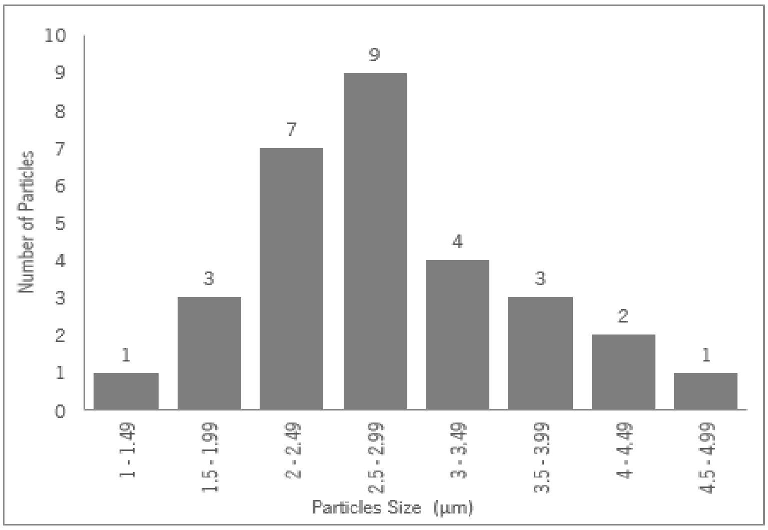


Figure 51. Histogram of Ni particles size distribution obtained from 30 measurements made to the particles pulverized on the substrate surface.

Table 8. Average diameter measured from the Ni particles pulverized on the substrate surface (30 measurements).

Ni particles pulverized on the substrate	
Average particles size (µm)	2.8±0.83

According to the results obtained it is possible to verify that the Ni micro particles dimensions stays under the <10 µm as indicated by the MERCK® suppliers.

In figure 52, are presented the average diameters of the Ni particles found in the solder joint after the Reflow soldering process (already seen above). Then, these results are compared with the diameter of the Ni particles added on the substrate.

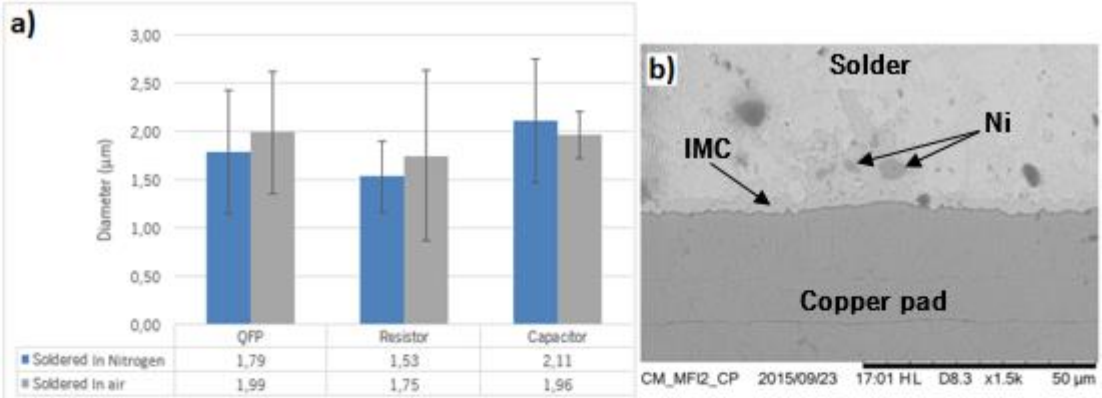


Figure 52. a) Represents the average diameter from the Ni particles added on the PCBs surfaces measured after the Reflow soldering process in N_2 and in Air atmosphere. b) Represents an example a Ni particle found in a sectional cut analyzed.

Analyzing the results obtained from the Ni particles present in the solder joint it is possible to verify that the mean diameters, about 2 µm, are similar. The fact that the standard deviation obtained is bit high can be explained by the different particles sizes or presence of possible agglomerations of Ni present, where the measurements were made. This contributes to higher values of Ni particles diameter.

Comparing the average diameters of the Ni particles present in the solder joint with the average diameters before the soldering process, it is possible to verify a decrease of the values. A reduction was verified from 2.8 µm to about 2 µm in all the conditions tested. This may prove that the reaction of the Ni particles with the solder during the Reflow happened. Thus, during this reaction Ni was consumed by the solder forming an intermetallic around this added particles.

4.6 University – Addition of Ni Particles

In order to have a more detailed study to compare with the results obtained at Bosch, tests were performed at the University and the following results were obtained. The tests consist in adding "2wt% Ni flux" on PCB substrates (coated with Sn) and soldering at different temperatures, different atmospheres (inert and oxidant) and different solders.

4.6.1 SAC405 and SAC305 Melting Temperatures

First in order to understand the influence of soldering with an oxidant atmosphere a thermal analysis to SAC405 and SAC305 solders were made to evaluate the melting temperatures of each one and each solder sample was tested in the TGA-DTA equipment. A thermal cycle was used with a heating up to 250°C, followed by a stage of 12 seconds. Three heating rates of 5, 10 and 30°C per minute, were tested.

After analyzed, the results obtained of the TGA-DTA graphics, in table 9 are presented the average melting temperatures of each solder tested in Argon and in Air atmospheres.

Table 9. Melting temperatures of the SAC405 and SAC305 tested in an inert and oxidant atmosphere at heating rates of 5, 10 and 30°C per minute.

	Temperature (°C)					
	SAC405			SAC305		
Heating rate (°C/min)	5	10	30	5	10	30
In Argon	217.52	218.06	222.58	217.15	220.77	225.27
In Air	216.74	218.55	222.78	217.45	218.72	225.21

Analyzing the results above it is possible to verify that there is no significant difference in the melting temperatures of each solder when heated in Argon or in an Air atmosphere. It is also possible to see that the melting temperatures values are in accordance with the datasheet provided by Heraeus®, supplier of these solders.

The slightly difference between the values obtained, can be explained by possible measuring errors that can occur during the tests, or by the tolerances of the test. This difference can also be caused by external factors, like existent impurities in the samples or in the equipment.

Therefore it is possible to say that soldering in Argon or in Air do not influence the melting temperatures of these two solders. Thus, it is possible to use the same thermal cycles for each kind of atmosphere and solder used.

4.6.2 Substrates With and Without Ni Particles Soldered With SAC405

After the "Reflow" soldering, in an inert and oxidant atmosphere, simulated in the TGA-DTA furnace, are represented the results obtained for each condition utilized. Thus, in figure 53 are presented some SEM images as an example of the aspect of the solder droplet obtained after the soldering process, at different temperatures.

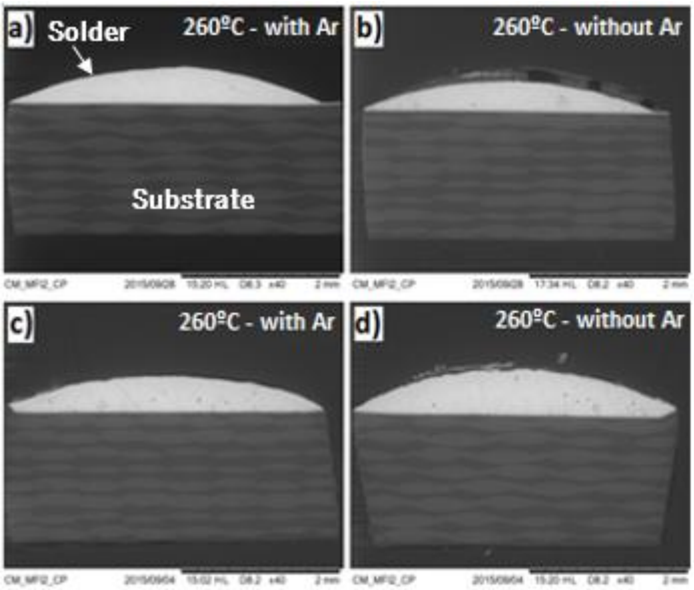


Figure 53. Normal substrates soldered at 260°C (a) and (b), and substrates soldered with “2wt% Ni flux” added (c) and (d), at different atmospheres, in Argon and in Air (without Ar).

From the above images it is possible to verify that the soldering happens, and in a qualitative analysis, it is possible to say that the solder appears to present a good wetting independent of the atmosphere. Analyzing the images of the substrates with Ni particles, it is possible to verify that there is no significant difference on the solder aspect. From the images obtained of the other soldering conditions as shown in appendix IV, the results of the solder aspect and geometry are very similar.

According to the performed tests, it was possible to solder at 220°C and 230°C when Ni particles were added to the PCB. Without the Ni particles, the lower temperature that was possible to solder was 240°C.

Nickel Particles

To analyze the presence of the Ni particles added initially to the substrate with the flux, an elemental mapping was made to the sectional samples cut. Thus, in figure 54 are presented some SEM images obtained where it is possible to evaluate the presence of Ni particles in the solder.

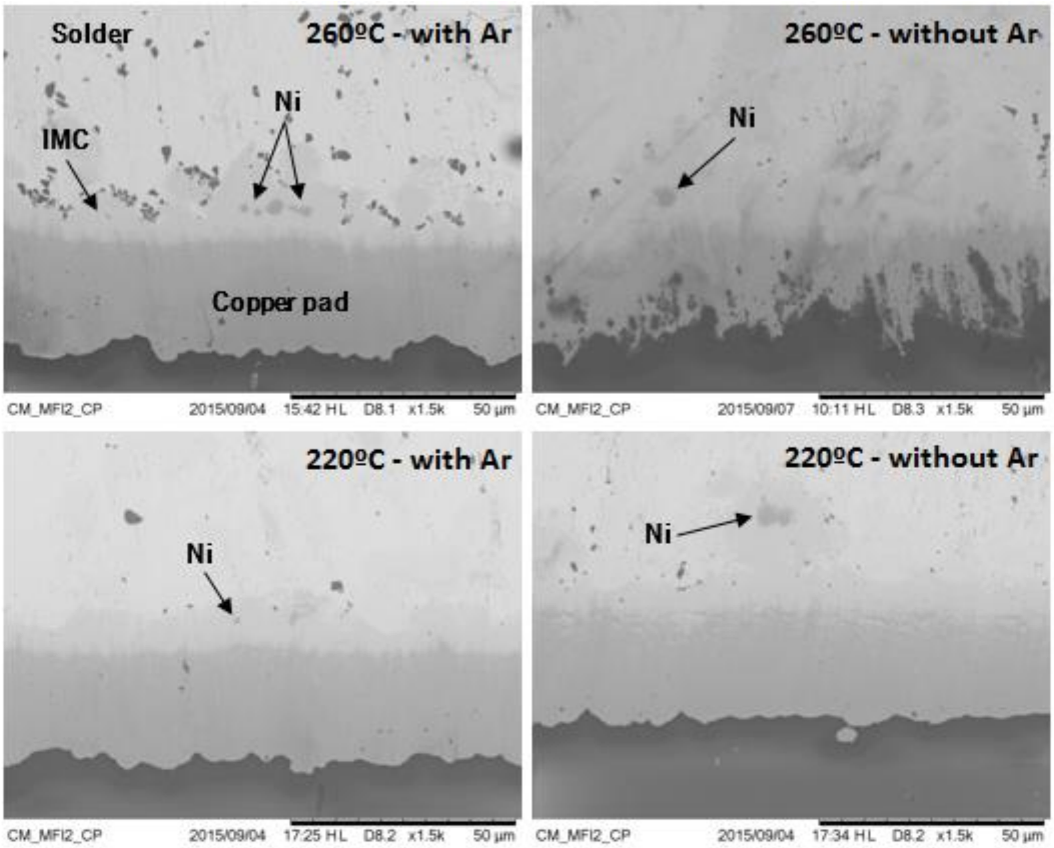


Figure 54. SEM images of some substrates with Ni particles soldered with SAC405 in different temperatures and atmospheres, in Argon and in Air (without Ar).

According to the SEM images presented above and at appendix V, it is possible to verify that these particles are located inside the intermetallic layer. Was verified that these particles are along of each sectional cut analyzed. It is also possible to see that there exists an intermetallic layer around these particles as already seen at the Bosch results. So, as already seen at the Bosch results, it is possible that during the soldering process can be formed a Cu-Ni-Sn intermetallic due to the possible reaction of the Ni particles with the Cu-Sn IMC and solder [40].

In figure 55 are presented the average diameters of the Ni particles found in the solder with the soldering tests realized. Then, these results are compared with the diameter of the Ni particles already measured at Bosch, but instead of utilizing a pulverization technique, Ni particles were applied via a drop of flux.

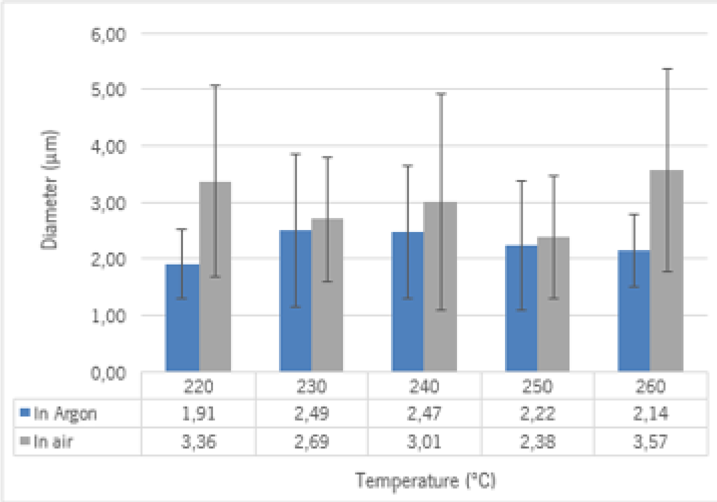


Figure 55. Average diameter from the Ni particles added on the substrates surface, soldered with SAC405 in Argon and in Air atmospheres.

Analyzing the results obtained it is possible to verify that the diameter values after measurement are similar when soldering in Argon, about 2 µm, and slightly higher when soldering in Air. This may be explained by the fact of the Ni particles reaction during the test, may be slower when soldered in an Air atmosphere. The high standard deviation values obtained may be explained by the different particles sizes or the presence of existent agglomerates Ni particles, and the measurement tolerances. Thus, with the existence of large amounts of agglomerates, the final diameter average of the Ni particles is bigger than it is in reality. These agglomerates can be associated to the method of adding Ni on the PCBs surface.

On the other hand, according to results from soldering in Argon, it is possible to verify a reduction of the 2.8 µm to about 2 µm. And as already seen at the Bosch results, this may prove that the reaction of the Ni particles with the solder happened, and the Ni is slightly consumed. However, the Ni particles added to the substrates soldered in Air also reacts with the solder because it is possible to see an intermetallic layer around these particles.

Intermetallic

Now to understand better the influence of using an inert or oxidant atmosphere and evaluate the influence of the Ni particles in the soldering process, the intermetallic layer formed will be studied.

After re-polishing the samples of SAC405 soldered with "2wt% Ni flux" in different atmospheres, the intermetallic thickness in three zone of each sample were measured (beginning, middle and end). In figure 56 are represented the average thickness values measured from the intermetallic layer of each soldering condition.

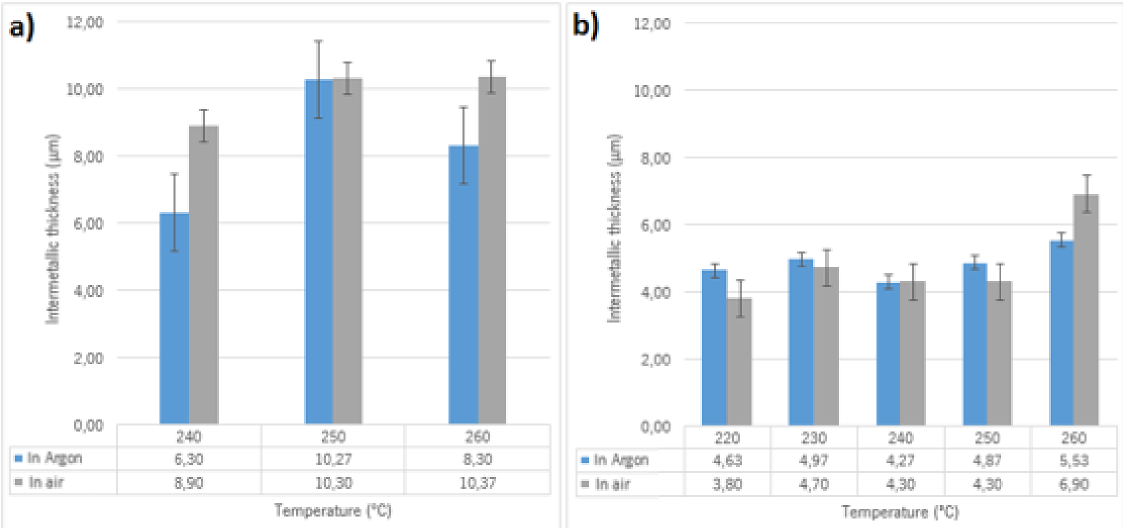


Figure 56. Thickness average values of the intermetallic layers measured from the SAC405 samples soldered at different atmospheres: a) normal substrates; b) substrates with "2wt% Ni flux" added.

According to the results obtained and taking into account possible errors resulting during thickness measuring, it is possible to see immediately that the temperature and presence of Ni influence the intermetallic thickness.

Looking at the results of the normal substrates soldered it is possible to verify that, independent of the atmosphere, the intermetallic thickness increases with the increasing of temperatures. This can be explained by the fact that with higher temperatures the reaction of the solder with the substrate copper pad is higher, so the intermetallic grows. The slightly differences in the values of soldering in different atmospheres may be explained by the process, parameters, materials and measurement tolerances. The standard deviations are related to the intermetallic irregular morphology.

Looking at the results of the substrates soldered with Ni particles added on the substrate surface, as the normal substrates soldered, the intermetallic thickness increases with the increasing of temperature. It is also possible to see that there is no significant difference when soldering in an inert or oxidant atmosphere.

Comparing the results, it is possible to verify that soldering without adding Ni, the intermetallic grows between the 6.3 µm to 10.3 µm, while soldering in the same conditions but adding Ni in the flux, intermetallic grows less, between the 3.8 µm to 6.9 µm. The less thickness of the intermetallic may be explained by the fact that, the presence of the Ni particles between the copper pad and the solder paste, during the reflow process, may act as a chemical and physical barrier between the pad and solder. As a result, the solder does not stay directly in contact with the copper pad suppressing the consumption of copper (of the pad) and reducing the intermetallic thickness. Thus, the intermetallic grows around the Ni particles, and in those areas, the copper pad thickness is higher comparing to the areas where there is no Ni particles.

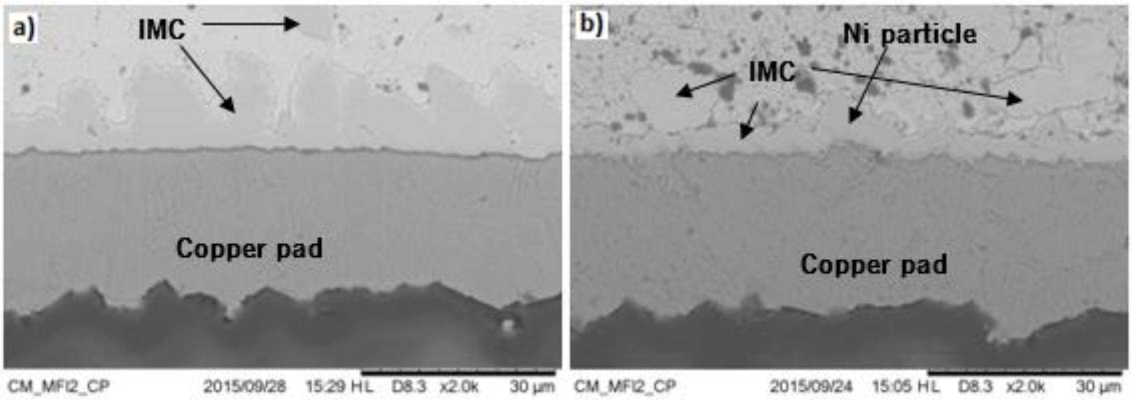


Figure 57. SEM image examples of the resulting intermetallic layer of soldering SAC405 on normal substrates soldered (a) and on substrates with Ni particles added (b), in the same conditions.

In figure 57 it is possible to see that the intermetallic layer of the substrates solder without Ni particles are higher, then the substrates soldered with Ni particles. It is also possible to verify that the copper pad thickness is slightly higher when Ni particles exist on its surface.

Finally and according to the literature, the fact that the solder joint of the substrates normal soldered has a higher IMC thickness, it may be more brittle than the substrates soldered with Ni added to it. This may happen because, with higher IMC formation, more probability of the bonding being brittle.

4.6.3 Substrates With and Without Ni Particles Soldered With SAC305

In order to understand better the influence of adding Ni on the soldering process, this time it is tested with other solder, SAC305.

In figure 58 are presented the same SEM images with an example of the aspect of what was obtained after the soldering process at different temperatures.

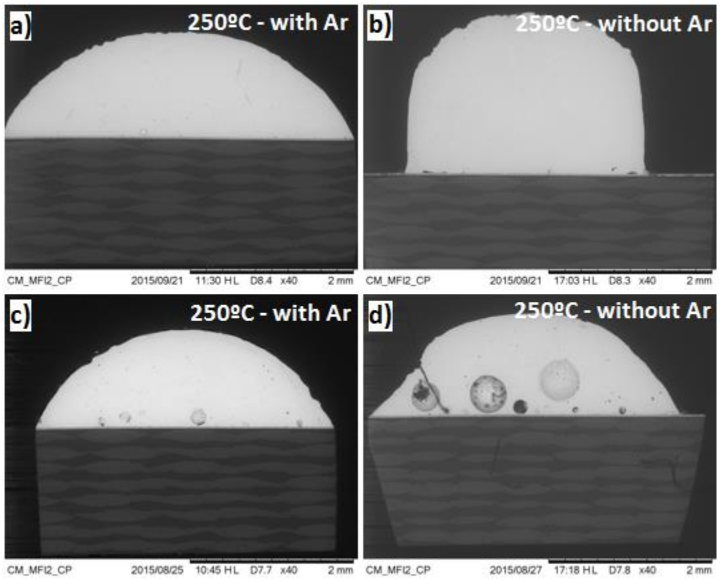


Figure 58. Substrates soldered at 250°C: normal substrates (a) and (b); substrates soldered with Ni particles added (c) and (d), at different atmospheres, in Argon and in Air (without Ar).

From the above images and from appendix VI it is possible to verify that the soldering happens. It is possible to verify a big difference between the samples soldered in Argon and in Air atmospheres. This can be justified by the fact that soldering in an oxidant atmosphere, oxides are formed on the surface of the pad and the melted solder, decreasing wetting. Thus, the final aspect of the solidified solders, are very different. These solder joints obtained present a worst aspect comparing to the solder joints obtained from solder with SAC405 (SAC405 is a solder paste with solder balls with flux). This way, SAC405 has flux acting during the soldering process, while SAC305 only has flux acting before the soldering process starts, and during the solder process there is no flux acting. This way, solder with SAC305 is more difficult.

In these results obtained, as already verified at SAC405 results, it was possible to solder at 230°C when Ni particles were added to the PCB. Without the Ni particles, the lower temperature that was possible to solder was 240°C.

Nickel Particles

As already studied in the SAC405 results, the presence of Ni particles in the solder after soldering it is analyzed. In figure 59 are presented some SEM images obtained where it is possible to evaluate the presence of Ni particles after soldering SAC305 with the Sn coated substrates.

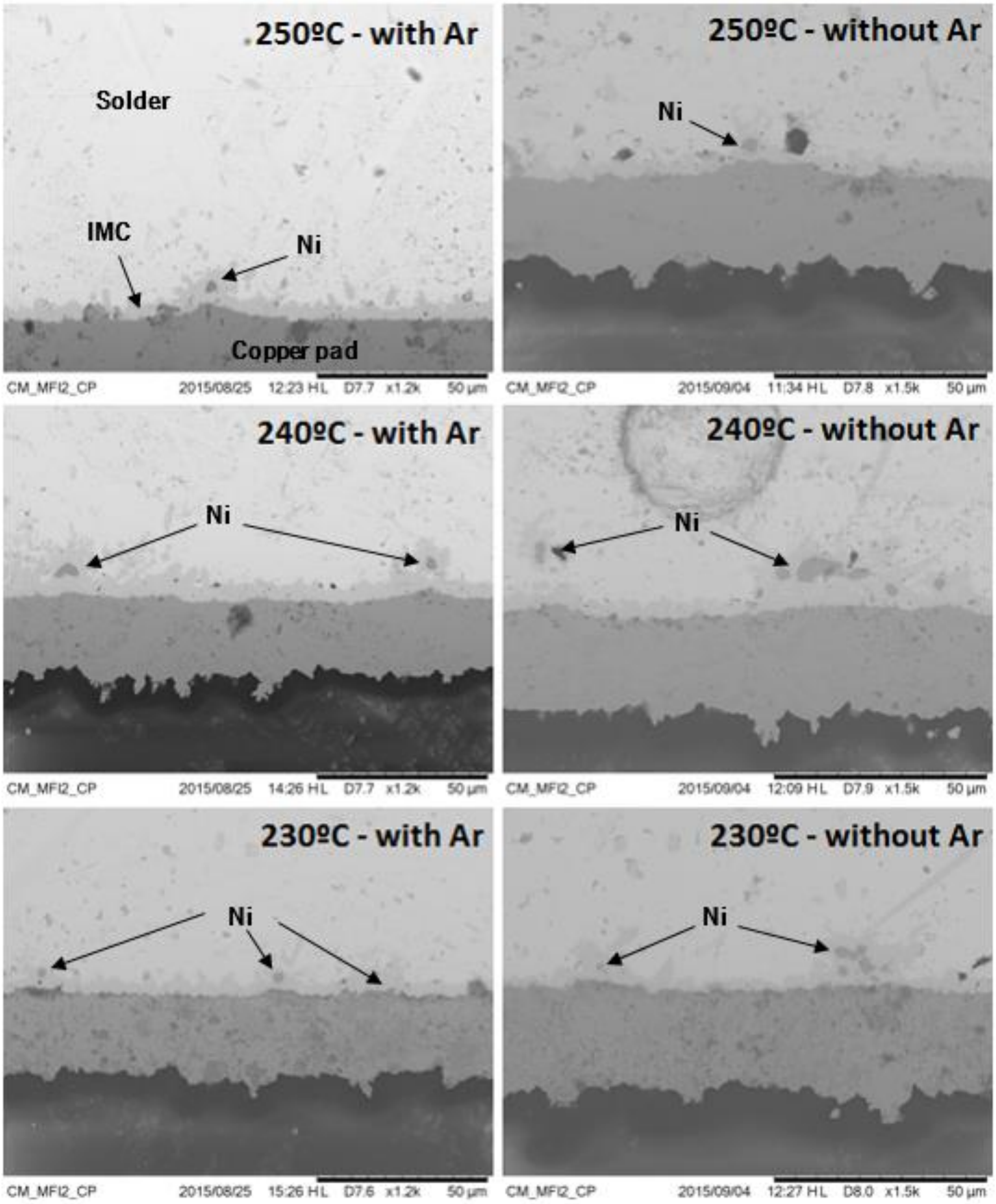


Figure 59. SEM images of some substrates with Ni particles soldered with SAC305 in different temperatures and atmospheres, in Argon and in Air (without Ar).

According to the SEM images presented above, it is possible to verify that these particles are located inside the intermetallic layer. It is also verified that these particles are along of each sectional cut analyzed. It is also possible to see that there exists an intermetallic layer around these particles. So, as already seen at Bosch and SAC405 results, it is possible that during the soldering process the Ni particles can react with the Cu-Sn IMC and the solder forming a Cu-Ni-Sn IMC [40].

The boundaries between the copper, IMC and the solder were studied. It can be seen that Ni particles are inside the intermetallic, and under these particles, the copper pad thickness is higher comparing with the remaining areas of the pad. This indicates that Ni may have acted as a chemical and physical barrier to copper consumption during the soldering reactions.

In figure 60 are presented the average diameters of the Ni particles found in the solder the soldering tests performed. Then, are compared with the diameter of the Ni particles already measured at Bosch.

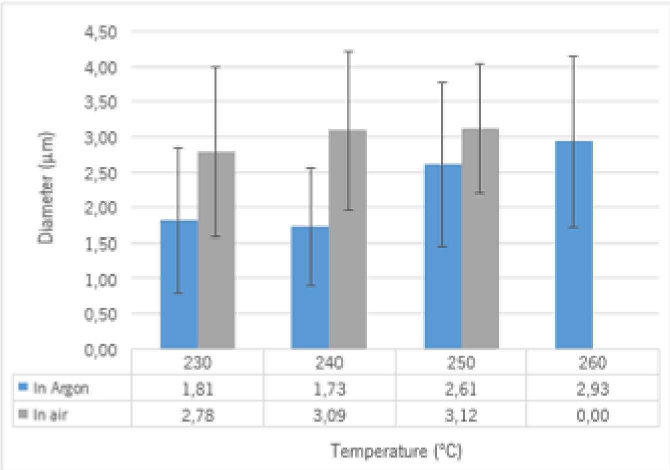


Figure 60. Average diameter from the Ni particles added on the substrates surface, soldered with SAC305 in Argon and in Air atmospheres.

Analyzing the results obtained it is possible to verify that the diameter values are slightly different at different temperatures and atmospheres used. The diameters measured, are between the 1.73 µm to 3.09 µm. So, as the average Ni particle add 2.8 µm, it is possible to say that exist Ni particles agglomerated exist, as already seen in previous cases. This can also be supported by the higher standard deviation values. According to these results it is possible to say that, as the Bosch and SAC405 results, the particles may react with the Cu-Sn IMC and the solder, and Ni is slightly consumed.

Finally it is possible to verify, even without finding Ni in the sample soldered at 260°C, that Ni particles present higher diameters when soldering in Air. Disregarding the agglomerations and measurement tolerances, this may be explained by the fact that with and oxidant atmosphere, the reaction may be slower, and in this way, the Ni particles are less consumed, presenting higher diameters.

Intermetallic

The intermetallic thickness of the SAC305 samples soldered with and without "2wt% Ni flux", in an inert and oxidant atmosphere, was measured. In figure 61 are represented the average thickness values measured in three zone of each sample (beginning, middle and end), from the intermetallic layer of each soldering condition.

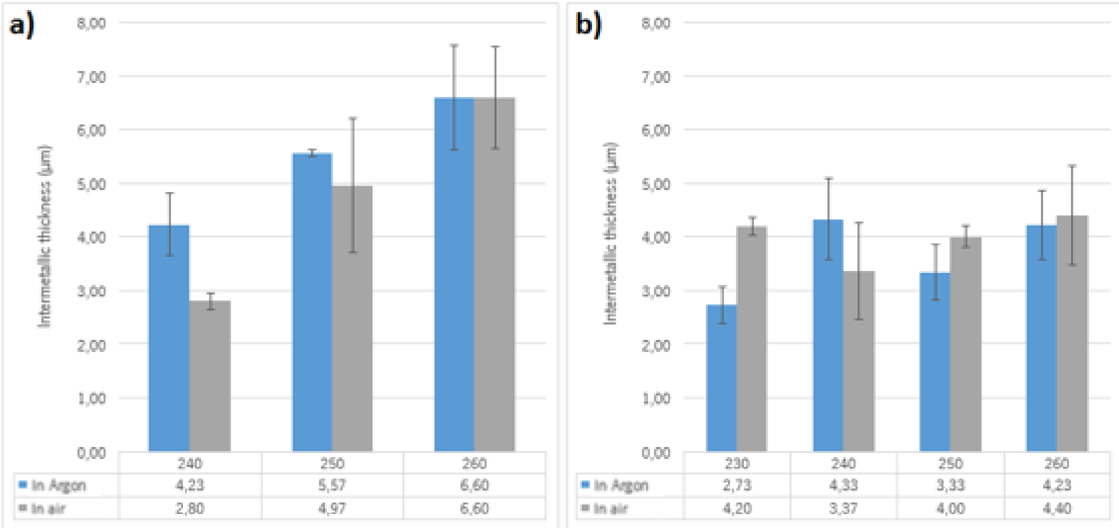


Figure 61. Thickness average values of the intermetallic layers measured from the SAC305 samples soldered at different atmospheres: a) normal substrates; b) substrates with "2wt% Ni flux" added.

According to the results obtained and taking into account possible errors resulting during thickness measuring, it is possible to see immediately that the temperature and presence of Ni influence the intermetallic thickness.

The results of SAC305 present the same tendency of the results obtained for the SAC405 results, but the intermetallic values measured are slightly smaller. This may be explained by the fact of using a different solder composition and for being a solder compact alloy instead of a solder paste.

Looking at all the results it is possible to verify that, independent of the atmosphere, the intermetallic thickness increases with the increasing of temperatures. As already explained, this may happens because with higher temperatures the reaction of the solder with the substrate copper pad is higher, so the intermetallic grows. Although, the slightly differences in the values of soldering in different atmospheres may be also explained by the process, parameters, materials and measurement tolerances. The standard deviation may be explained by the formation of an irregular intermetallic.

Comparing the results, it is possible to verify that soldering without adding Ni, the intermetallic grows between the 2.8 µm to 6.6 µm, while soldering in the same conditions but adding Ni with the flux, intermetallic grows between the 2.73 µm to 4.40 µm.

As already seen in SAC405 results, the intermetallic thickness of the sample soldered with Ni particles is smaller. This may happened because the presence of the Ni particles between the copper pad and the solder paste, during the reflow process, may act as a chemical and physical barrier between the pad and solder. The solder does not stay directly in contact with the copper pad suppressing the consumption of copper (of the pad), reducing the intermetallic thickness. Thus, the intermetallic grows around the Ni particles, and in that areas, the copper pad thickness is higher comparing to the areas where there is no Ni particles.

As it can be seen in figure 62 that intermetallic layer of the substrates solder without Ni particles are higher and more irregular, then the substrates soldered with Ni particles, and the copper pad thickness is slightly higher when there is a Ni particle on its surface. It is also possible to verify that under the Ni particles, the copper pad thickness is higher comparing to the other areas. This can show that the Ni particles during the soldering process may act as a chemical and physical barrier between the pad and solder, suppressing the copper consumption.

From the results of soldering without adding Ni particles, it is possible to see that in addition of having higher intermetallic layers, the IMCs starts to migrate to the solder.

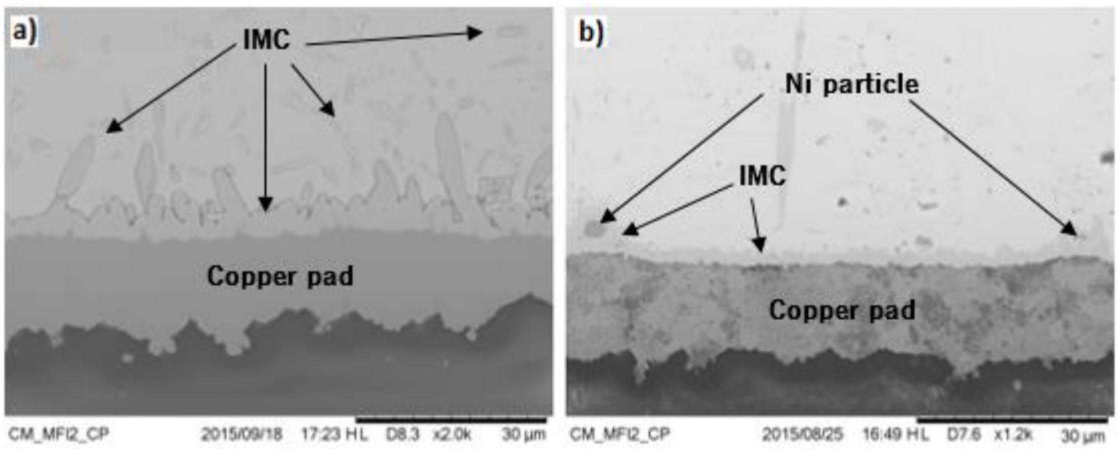


Figure 62. SEM image examples of the resulting intermetallic layer of soldering SAC305 on normal substrates soldered (a) and on substrates with Ni particles added (b), in the same conditions.

CHAPTER 5

CONCLUSION AND FUTURE WORKS

5.1 Conclusion

This project allowed to understand the fundamental processes and all the concepts which lie behind the production of the Printed Circuit Boards, such as components mounting, solder characteristics, soldering processes and atmospheres, quality inspection, among others. This project also allowed to understand how a company works from the raw material orders, the production planning and finally the production. At Bosch Car Multimedia internship with the involvement with the responsible persons of the area, such as technicians and engineers, as well as the interaction with the order of the material and with the production lines allowed to acquire knowledge and experience that would not be possible to acquire at the university.

The results obtained from the project and after their analysis, it is possible to obtain some conclusions about the tests performed at the company (Bosch project departments and production line) and with laboratorial work (at the University of Minho).

Regarding the tests at Bosch Car Multimedia:

- According to the SPI results and obtained height, area and volume solder measurements, there is no differences in the solder printing for all the PCBs printed, even the PCBs with "2wt% Ni flux" on the surface;
- According to the AOI results obtained, it was verified that no error has been detected in all the PCBs analyzed. Only pseudo-errors were detected. It was verified, that on the soldering in an Air atmosphere, these pseudo-errors tripled comparing to the pseudo-errors detected for the PCBs soldered in Nitrogen;
- From visual inspection, all PCBs were accepted. From the 16 PCBs analyzed in detail at the lab, no defect was detected;
- According to the X-ray inspection performed to the SOT components, it was verified that the SOT soldered in an atmosphere of Nitrogen presents less voids comparing to those soldered in Air;

- Analyzing the solder joint geometry, it was verified that the PCBs/components soldered in Nitrogen presents higher heights on the solder joint, concave solder fillets, better wetting and spreading. Those PCBs/components soldered in Air presents less solder joint heights, solder fillets less concave, higher contact angles, and wets less the component pin (lead);
- According to the IPC-A-610D standard, the fillet height and solder thickness between the component's pin and copper pad, it was verified that the solder joints satisfy the standard requisites;
- From the chemical constitution elemental mapping it was verified that: the constitution of the solder is principally of Sn, Ag and Cu; the PCBs pad are formed by Cu; and the component's pin formed by Cu and has a coating of Ni. This elemental mapping together with the SEM images, also allowed to verify the presence of the Nickel particles added, present in the solder joint are inside of the intermetallic layer;
- About the intermetallic layers, was verified the formation of the IMCs solder-copper pad, and the IMCs solder-components pin in all the samples studied. It was also verified that the soldering atmosphere does not influenced the intermetallic thickness, and the results obtained were in agreement with the Bosch specification;
- According to the Ni particles morphology and size, it was verified the presence of some agglomerations when pulverized into a surface, and measured an average particle diameter of 2,8 μm. After soldering, it was verified that the Ni particles size was identically in all the atmospheres used, and presents a less particles size than the measured size before the soldering process. Therefore, the Ni particles reacted with the solder, being consumed and forming an IMC around the particles added.

Regarding the tests at the University:

- The SAC405 and SAC305 solders, soldered with an atmosphere of Argon or Air do not influence their melting temperatures;
- The Ni particles addition to the PCB reduces the temperatures that was possible to solder, it was possible to solder at 220°C and 230°C, when without Ni particles, the lower temperature that was possible to solder was 240°C.
- The Ni particles added on the substrate surface, after soldered with SAC405 and SAC305 solders, are located inside the intermetallic layers and present identical average sizes. The

size under and above the 2,8 μm, means that the Ni particles reacted with the solder but also means the existence of agglomerations;

- The Ni particles are bigger for the SAC405 and SAC305 solders when soldered in Air, indicating that when soldering in an oxidant atmosphere the reaction between these particles and the liquid solder might be slower;
- Independently of the atmosphere, for the SAC405 and SAC305 solders, the intermetallic thickness growths with the temperature increase;
- Independently of the atmosphere, it was verified that the presence of Ni reduces the intermetallic thickness, reducing the consumption of copper under the zones where these particles are located.

Finally, from all the results obtained, it is possible to conclude that, for the tested conditions, soldering is possible with one Reflow process in Air atmosphere, ensuring the Bosch standard specifications and without finding defects. It is possible to reduce the costs with N_2, but further investigations, as the reliability tests, have to be made to support these first results.

The Nickel particles addiction on the PCBs surface according to the results obtained, reduces the soldering temperatures, reduces the copper pad consumption, that may be possible to reduce the production costs, and may increase the reliability of the solder joint by decreasing the fragility of the intermetallic layer. But some other investigations have to be made to confirm the influence of Nickel in the process.

5.2 Future Works

Due to the high importance of this study for the PCBs soldering area it is necessary to have a depth knowledge of the conditionings that the new variables introduced can bring. In order to support the conclusions reached and clarify the influence of Nickel in the soldering process, the following future works are suggested:

- Perform reliability testing to the produced PCBs;
- Perform mechanical tests to the produced PCBs to evaluate the bonging strength between the PCB and components;
- Soldering tests but with two Reflows in an Air atmosphere;
- Test other PCBs surface finishes, as HASL, OSP and ENIG;
- Tests to verify in detail if the Ni diffuse into the solder;

- Accomplish the same soldering tests with addition of different percentage of Ni micro particles in the flux to add on the PCBs surface.

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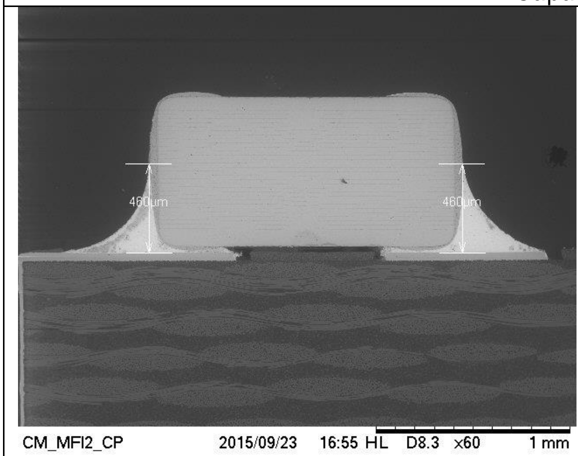
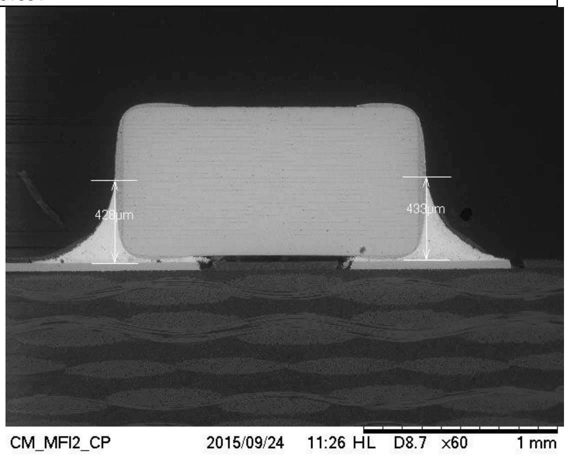
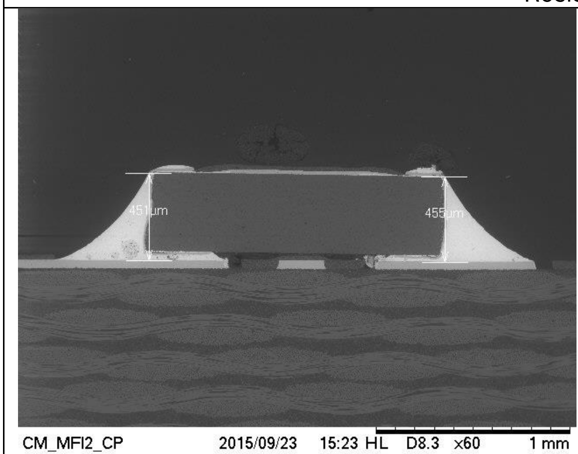
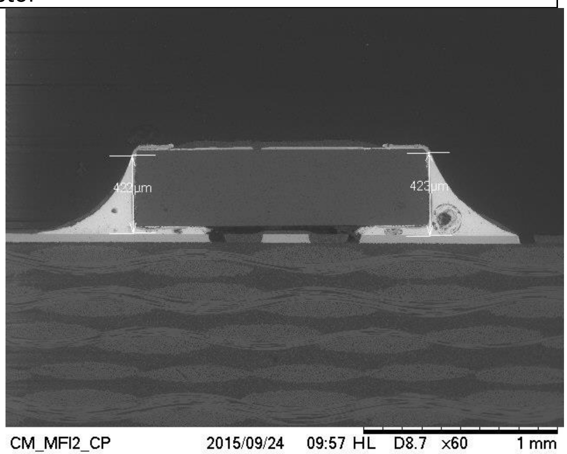
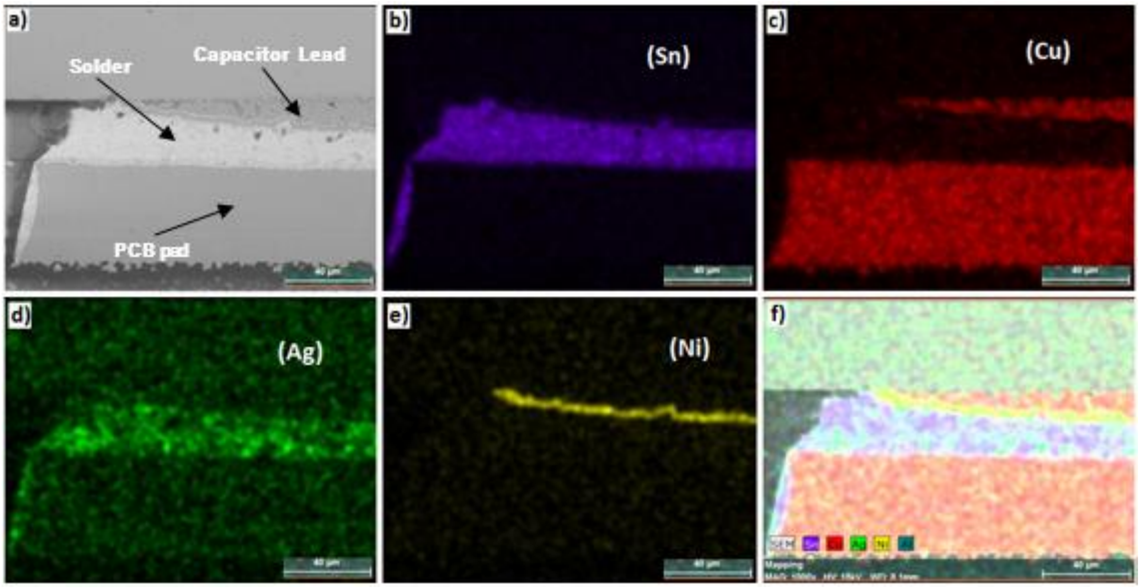
SEM images examples of the heights from the Capacitor and Resistor soldered in N_2 and in Air atmospheres.

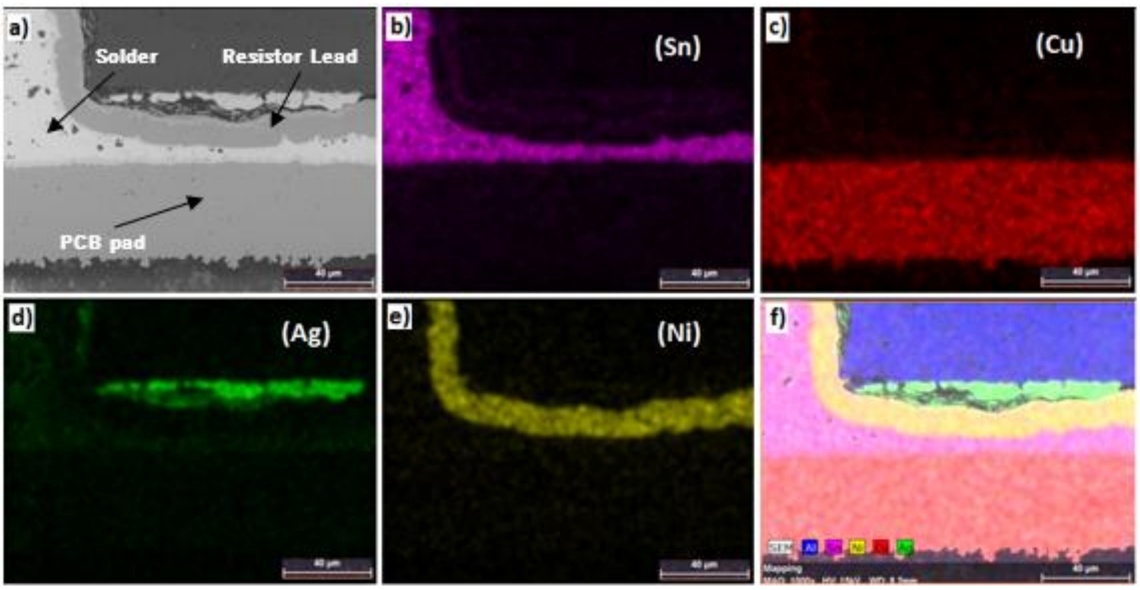
<table>
<tr><th colspan="2">Soldered in Nitrogen</th><th colspan="2">Soldered in Air</th></tr>
<tr><td colspan="4">Capacitor</td></tr>
<tr><td colspan="2">
</td><td colspan="2">
</td></tr>
<tr><td>Left lead: 460 µm</td><td>Right lead: 460 µm</td><td>Left lead: 428 µm</td><td>Right lead: 433 µm</td></tr>
<tr><td colspan="4">Resistor</td></tr>
<tr><td colspan="2">
</td><td colspan="2">
</td></tr>
<tr><td>Left lead: 452 µm</td><td>Right lead: 455 µm</td><td>Left lead: 422 µm</td><td>Right lead: 423 µm</td></tr>
</table>

APPENDIX II

SEM images of the solder joint formed at the Capacitor right lead, soldered on a normal PCB in a Nitrogen atmosphere (a) and corresponding elemental maps Sn (b), Cu (c), Ni (d), Ag (e), and all maps combined (f).

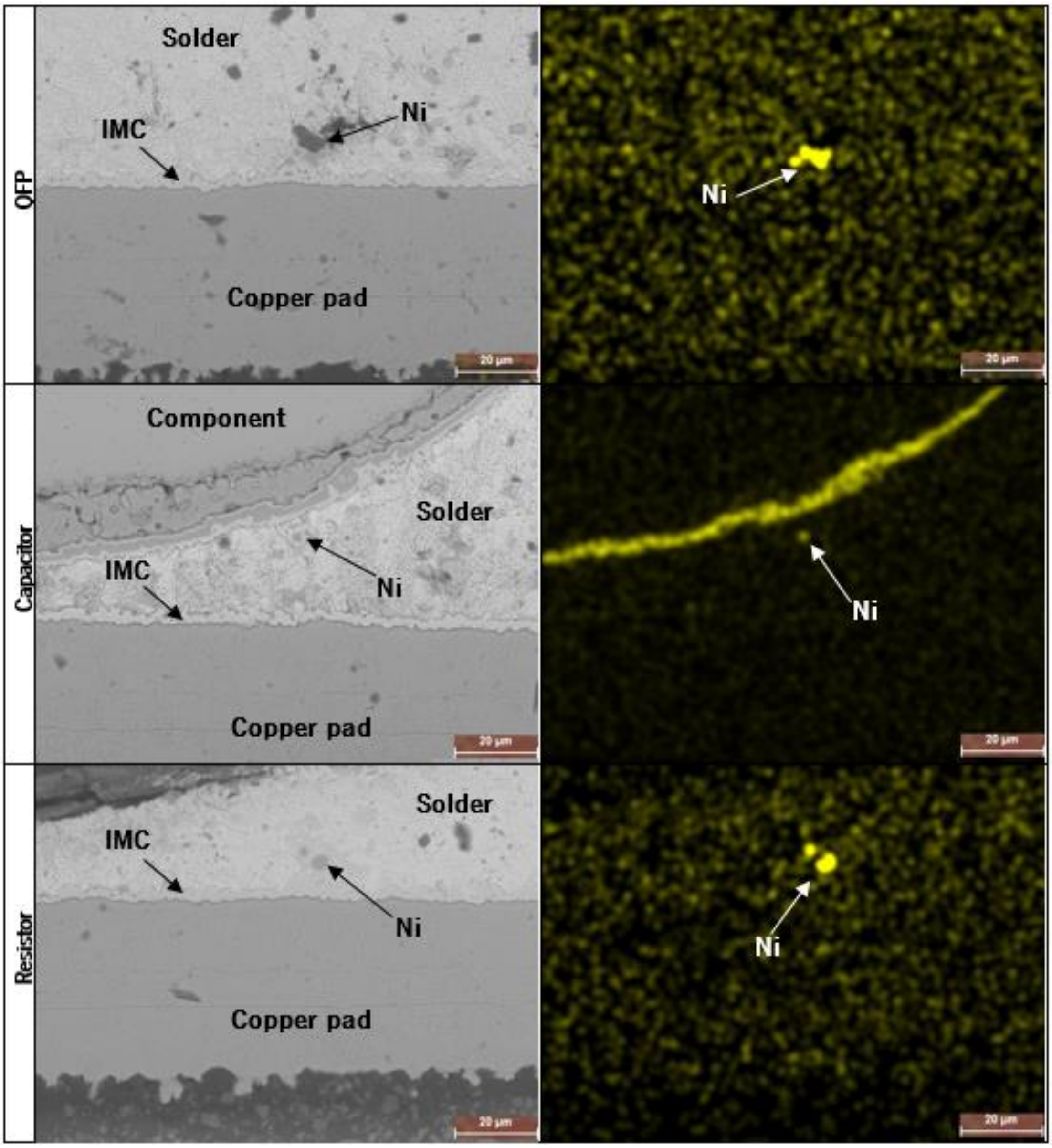


SEM images of the solder joint formed at the Capacitor right lead, soldered on a normal PCB in a Nitrogen atmosphere (a) and corresponding elemental maps Sn (b), Cu (c), Ni (d), Ag (e), and all maps combined (f).



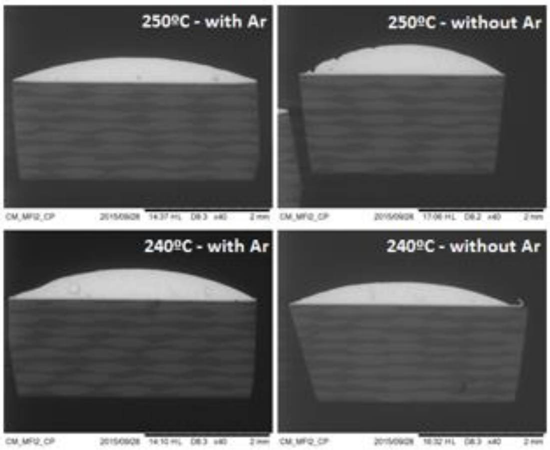
APPENDIX III

SEM-EDS elemental mapping of the QFP, Capacitor and Resistor left pin (lead), soldered on the board with “2wt% Ni flux” in an Air atmosphere.

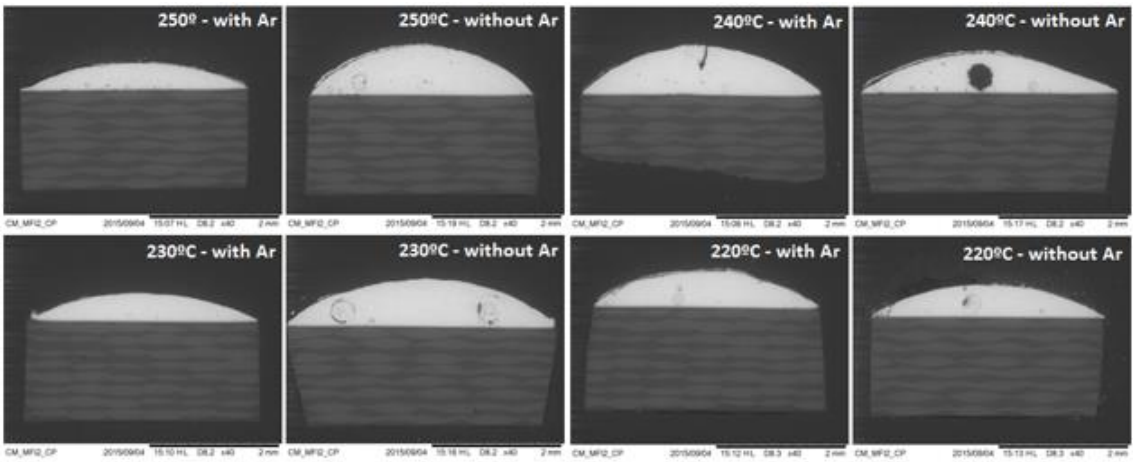


APPENDIX IV

Substrates with SAC405 at different temperatures and atmospheres, in Argon and in Air (without Ar).

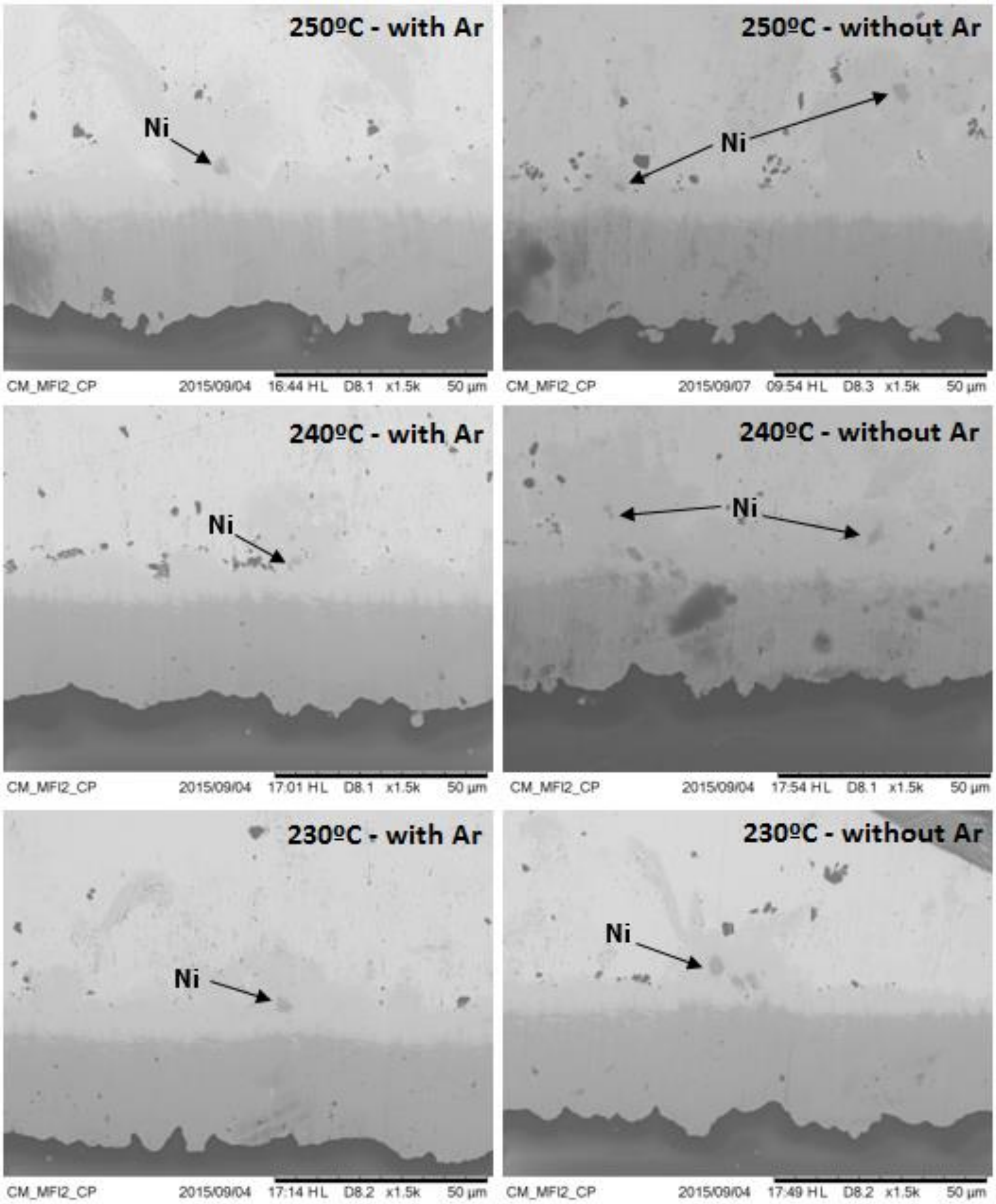


Substrates with "2wt% Ni flux" soldered with SAC405 at different temperatures and atmospheres, in Argon and in Air (without Ar).



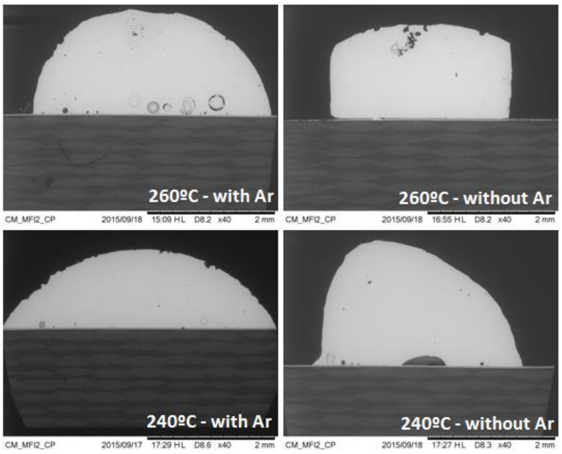
APPENDIX V

SEM images of some substrates with Ni particles soldered in different temperatures and atmospheres, in Argon and in Air (without Ar).



APPENDIX VI

Substrates with SAC305 at different temperatures and atmospheres, in Argon and in Air (without Ar).



Substrates with “2wt% Ni flux” soldered with SAC305 at different temperatures and atmospheres, in Argon and in Air (without Ar).