

**STRUCTURAL TRANSFORMATIONS OF LOW TEMPERATURE,
PRESSURELESS SINTERED SILVER NANOPARTICLES FOR DIE
ATTACH INTERCONNECTIONS**

By

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ABSTRACT

The new generation of wide-bandgap semiconductor devices has proved superb performance among high power electronic devices, demonstrating total functionality at temperatures above 500°C. However, they are limited by current die attach technology which mechanically secures them just up to ~250°C. Reliability problems due to thermal stresses and thermal stability are prevalent reasons. This project proposes a die attach solution using pressureless sintering of silver (Ag) nanoparticles to produce a compact material at relatively low processing temperatures, but with high operating temperature capabilities.

Formulating the Ag nanoparticles in a simple dispersant medium and subjecting the resulting paste to sintering tests at different temperatures, dwell times, and environments, was done for the understanding of its evolution mechanisms. Conclusive results were obtained through microstructural analysis and characterization, via SEM examinations, thermal evaluations, qualitative appraisal, and stereological analysis. An exhaustive analysis of the process was carried out from the nano to the macro length scale suggesting the criticality of the mesoscale, where functional interactions were linked. As result, a promising method is suggested by mixing different particles sizes, coating states, and environments, to enhance the sintering results at 300°C, so that a reliable die attach for harsh environments can be obtained.

RESUMEN

La nueva generación de dispositivos semiconductores de *bandgap* amplio ha probado un desempeño superior entre los dispositivos electrónicos de alta potencia, demostrando una funcionalidad total a temperaturas por encima de los 500°C. No obstante, ellos están limitados por la actual tecnología *die attach*, la cual se encarga de proveerles fijación mecánica sólo hasta ~250°C. Los causales principales de estas dificultades se le atribuyen a problemas de confiabilidad generados por esfuerzos e inestabilidad termal.

Este proyecto propone una solución para el *die attach* usando *sintering* de nanopartículas de plata (Ag) para producir un material compacto a unas temperaturas de procesamiento relativamente bajas, pero con capacidades de operación a altas temperaturas.

La formulación de nanopartículas de Ag en un medio dispersante simple y sometiendo la resultante pasta al *sintering* a diferentes temperaturas, tiempos de sostenimiento, y ambientes, fue hecha para la comprensión de sus mecanismos de evolución. Se obtuvieron resultados concluyentes a través del análisis y la caracterización micro-estructural, vía examinación en SEM, evaluaciones térmicas, valoración cualitativa, y análisis estereológico. Un análisis exhaustivo del proceso fue desarrollado desde la escala nano hasta la macro sugiriendo la criticidad de la meso-escala, donde las interacciones funcionales fueron convergentes. Como resultado, se sugiere un prometedor método por medio de la mezcla de diferentes tamaños, estados de surfactación, y ambientes, para mejorar los resultados del *sintering* a 300°C, de modo que se pueda obtener un *die attach* confiable para ambientes agresivos.

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LISTS OF ACRONYMS

1. DSC.....Differential scanning calorimetryA thermal characterization technique.
2. FUC.....Flaky uncoated.....A type of nanoparticle
3. HEP.....High power electronicsIndustrial devices for high power applications
4. SEMScanning electron microscopyCharacterization technique
5. SOC.....Spherical oleic coated.....A type of nanoparticle
6. SUC.....Spherical uncoated.....A type of nanoparticle
7. XRDX-ray diffractionCharacterization technique

1. INTRODUCTION

Most of the electronic devices like analog, digital, or radio frequency, have as main objective to represent and process information electronically; however, power electronics are configured for processes concerning to applications in control, distribution, and conditioning of power. High power electronics (HPE) play a very important role in control and conversion of electrical power, i.e. conversion from an electrical source to an electrical load in a highly reliable and efficient, but even cost-effective way. HPE are conceived for operations as energy storage, transmission, and conditioning, communications, computer systems, propulsion, and transportation [1–3]. HPE applications are vital in the performance of fuel combustion systems, high temperature manufacturing processes, deep-well drilling, hybrid and electric vehicles, more electric ships and planes, and outer space exploration [4–6].

Next sections will present information about the relevancy of semiconductors in the operation of HPE and the principal concerns affecting their performance. It will start from the main aspects of their assembly and fabrication, followed by the specific aim of this study which is to investigate how to overcome the actual deficiencies in electronic packaging of HPE.

1.1. From Si-based to Wide-bandgap devices in HEP

Chips play a major role in the topological, i.e. functional configuration, of electronic systems because they support basic components (diodes, transistors, among others.) that perform punctual but crucial tasks. Chips are made by micro-fabrication methods, using a die (single

crystal semiconductor) which is extracted from a wafer. Every year the demands of markets grow faster than fabrication methods can do; it means, consumers require applications which involve ever higher current densities, space and weight reductions, higher switching frequencies, high vibrating conditions, and high radiation exposure. These factors carry the functional properties of semiconductor dies to their limits, for example their junction temperature. It is known that for Si-based semiconductors the maximum junction temperature ($T_{j,max}$) is 150°C, limiting their operational integrity beyond that condition [5, 7].

It becomes necessary to either reduce the working temperature or increase the maximum allowable temperature of the semiconductors, to overcome the aforementioned hurdles. In recent decades, a new generation of wide-bandgap (WBG) semiconductor has demonstrated superb properties, thus promising to meet the demand of high power and high temperature applications. Silicon carbide (SiC) and gallium nitride (GaN) have shown higher performance levels [5, 7], when compared to available Si-based technologies: higher overall efficiency, greater electric breakdown voltage² capacity, and one of the most relevant characteristics, high thermal conductivity and stability. SiC devices have been demonstrated to operate up to 600°C, which is 4 times higher than Si-based devices; thus opening the possibility for WBG as a substantially reliable solution for high temperature electronic applications.

² Breakdown voltage: minimum voltage necessary to change from isolating to a conductive state.

1.2. Electronic packaging

The hierarchical structure of the electronic devices is based on conjugating the operation of elemental components through different topologies (functional disposition), as it is the case of chips (dies) to accomplish more complex functions; dies are conformed by basic components (transistors, resistors, diodes, etc.) and configured as discrete or integrated semiconductor devices (by specific fabrication methods), to accomplish either active or passive functions for specific tasks in the system.

Electronic packaging uses technologies, methods and a variety of materials to realize the physical setup for the system in order to perform: electrical signal interconnection; power distribution; mechanical and environmental protection, and heat dissipation of the components [8–10]. Appendix I shows some common materials used for different packaging tasks.

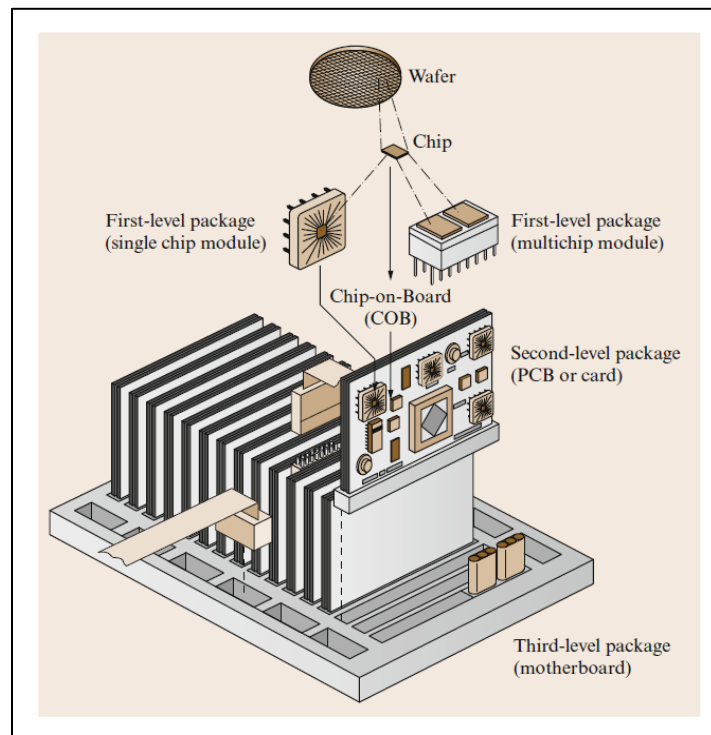


Figure 1. Exploited representation of the real electronic packaging levels in an assembly [9].

Figure 1 illustrates the classical hierarchy used for packaging in manufacturing processes of electronic devices. Packaging and fabrication move from devices within the chip (0th level), to chip attachment and wire bonding (1st level), to device interconnection into printed circuit assemblies (2nd level)), to mother board to mother board interconnections (3rd level)), passing through cabinet or subcabinets with multiple boards and a multi-cabinet arrangements (which can be considered as 4th and 5th levels of packaging, respectively).

As mentioned before, die attach is considered part of the first interconnection level and it takes care of securing chips to a substrate. Thus, considering the capacity of WBG to operate reliably at elevated temperatures, without the need of active cooling, it opens opportunities for in-situ applications of power electronics, where control modules can be located directly in close physical proximity to actuators. However, while this is a great accomplishment for HPE devices, it represents new challenges for die attach methods and materials to step forward and develop novel technologies that can withstand the ever increasing operating temperatures.

1.2.1. Die attach

Die attach deals with the packaging of one or more chips into a substrate, therefore it has the function of mechanically securing the chip while preventing it from detaching or fracturing over the operational lifetime of the system. Thus as an interface (see Figure 2), it has to provide a heat path for thermal management, with low electrical resistivity, and it should be a compliant connection between die and substrate [11, 12].

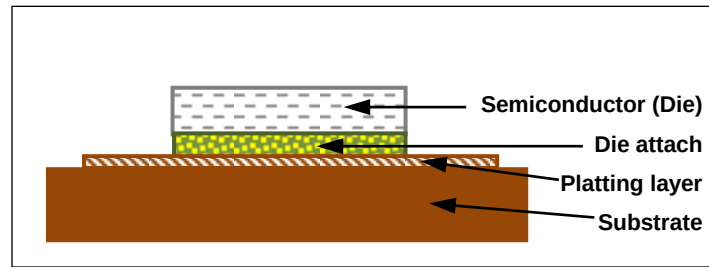


Figure 2. Basic structure of a die attach joint.

Die attachment has been traditionally performed using adhesives (based on metal filled epoxies) or solders to bond the die onto the substrate. High temperature electronics tend to use hard solders or brazes (due to their high melting points of $\sim 300^{\circ}\text{C}$ or above) for die attaching, since adhesives decompose at temperatures near 200°C , and the eutectic tin-lead solder melting temperature is too low (183°C) [13, 14].

The next section will discuss details of the die attachment methods and common materials.

1.2.2. Soldering

This method is the most common technique used in the industry, and it is based on using a single metal or metal alloy solder as joining element between the chip and substrate. By heat application, solder gets reflowed (melted and solidified) to produce a strong metallurgical bond between the component surface and the substrate³. For this method alloys can be off-eutectic or eutectics; preferably eutectic compositions are used owing to its low melting temperature and the lack of a pasty range during the process [17, 18].

³ A quite new technique is solid-liquid interdiffusion that has been proposed for HPE; actually with good results, but its drawbacks are still of concern for scientists [15, 16].

When the joint is intended for high temperature operational conditions or thermal cycling, it is desirable to use a solder material with a coefficient of thermal expansion (CTE) close to that of the substrate and die, to reduce thermal stresses generated during its life time operation [19, 20].

Common solders used (and still in use) for high temperature applications are based on highly concentrated (95 wt.% Pb or above) Pb-alloys; however due to the restriction of hazardous substances legislation (RoHS) banning the use of Pb from electronics there has been a move to Ag, Au, Cu, and Sn-based alloys. They can be in paste or wire form for this purpose. Appendix II shows a table with materials of common solder alloys along with some of their thermal properties and their composition [13].

Getting into the process, soldering starts with surface preparation, which encompasses cleaning and the application of a metallization layer where the substrate and the die are metal coated to maximize the affinity between their constituent materials with the solder metal. A second step is the application of the solder material to the substrate. When a paste is used, the solder is applied by stencil printing followed by the placement of the device. When reflow is used the whole assembly is heated above the melting temperature of the solder (at least 30°C above the liquidus temperature of the solder) so that upon solidification a metallurgical bond is achieved. It is worth noting here that for a system to withstand high temperature environments it must be interconnected with a high melting point material, which implies (if reflow is used) a processing temperature even higher. This is a major drawback for this traditional process, since processing temperatures could be very detrimental for the assembly; therefore a material/method that can be processed at a relatively low temperature but can survive reliably the high temperatures of the application is much needed.

Current soldering techniques include hand soldering, wave soldering, reflow soldering, and soft beam soldering or laser soldering. Current soldering techniques include hand soldering, wave soldering, reflow soldering, and soft beam soldering or laser soldering [13, 14, 18]. Despite of the technique the effectiveness of soldering depends on several factors:

- * *Wettability* is the capacity of a liquid like material to cover the surface of the solid material by a true interface contact; it is a crucial factor for getting the necessary solder diffusion during bonding. The surfaces to be joined must be free of contaminants in order to obtain a good wetting action, spreading shape of a reflowed droplet of solder material over the contact surface is usually taken as quality indicator.
- * For the case of *solder pastes*, it is common to prepare them with organic solutions to disperse and homogenize the solder metallic powder; that in combination with other agents forms the paste with its required rheological properties. These solutions, known as *fluxes*, together with the dispersing functions are intended for surface scrubbing and metal oxides reduction. In this way, fluxes get to improve the wettability of the solder by the elimination or inhibition of present or formed contaminants during the soldering process. A significant drawback of these fluxes is that often (there are some weak no clean fluxes available that may not work properly at high processing temperatures) residues need to be clean after the soldering process, however some traces may still remain. All these remnants could act as thermal and electrical isolators, thus representing potential defects for mechanical response; furthermore they tend to be hygroscopic thus becoming preferred oxidation sites [21].
- * *Surface metallization* is an additional tool used prior to the soldering process to enhance surface diffusion-adhesion behavior of solder-die and solder-substrate interfaces. It consists of thin or thick layers of metal deposited onto the joining surfaces to increase the adhesion

between the reflowed solder and the solid surfaces during the heating cycle. Other variety of metallization layer can be produced for chemical passivation in joined materials (see section 1.2.3).

- * *Thermal stability* is the capacity of the solder to not react, decompose in adverse substances or oxidize during thermal excursions. Such degradation could weaken the thermal and the electrical conductivities in the future, as well as the mechanical properties of the junction [13]. Grzybowski [14] presented an analysis of degradation solder materials at high temperatures.

1.2.3. Surface metallization

Metallization encompasses a variety of techniques for coating with metallic layers the surfaces to be in contact with the solder in the final assembly. They are intended to enhance the adhesion between the solder and non-metallic surfaces. Metallization layers also aims at the reduction in the CTE mismatch between solder and the material of the die and substrates. With a material's adequate Young's modulus selection, the metallization also increases the long term mechanical resistance to fatigue and creep of the joint during thermal excursions [13, 22]. Several materials including Ti, Cr, Au, and other metals including alloys, are actually employed for metallization layers [15, 18]. Appendix IV presents a comparison of thermomechanical properties of different materials used in metallization design for packaging [20].

Nonetheless, a good metallization preparation has to ensure an acceptable chemical stability thus reducing the oxidation and the undesirable formation of intermetallic compounds in the interfaces at high temperatures. Additional metallic layers, called *diffusion barriers*, have to be considered to impede the unwanted intermetallic formations and/or diffusion. The most

widely used materials for this purpose are W, Cr and Ni. Appendix V gathers the principal material used in UBM and their functional purposes.

Metallization methods includes physical vapor deposition (PVD), chemical vapor deposition (CVD), electroless deposition, and a novel and reliable technique, jet vapor deposition (JVD). Other available techniques, depending on the manufacturing schemes, are electroplating, stencil printing, solder ball bumping, micropunch, and solder jet (in-jet printing) [15, 23].

1.2.4. Thermal profile

The formulation of a joint between the die and the substrate by means of soldering (reflow) process requires three main steps: pre-heating, reflow or soldering, and cooling down; which together are referenced as the thermal profile. Each profile is customized (in time and temperature) based on the selected materials for the assembly.

In the pre-heating, the assembly temperature is gently increased to avoid abrupt gas formation and ejection (1 to 3°/s is a good range) until the boiling point of the solvents and the flux activation temperature is reached; afterwards an isothermal hold is employed to guarantee the evaporation of the remaining solvent, followed by quick temperature ramp (from 1 to 5°/s) until the reflow temperature is reached (typically 30°C above the liquidus temperature for a solder). In this second ramp some remaining flux and coating agents evaporate while the rest of additives burn out. During reflow the molten solder starts wetting and spreading. Afterwards, the package is slowly cooled down to reduce residual thermal stresses (see Figure 3).

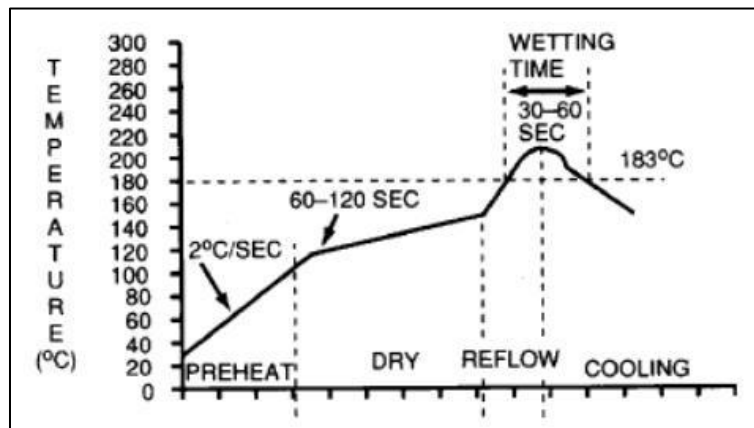


Figure 3. Typical industrial thermal profile for solder reflow. [24]

1.3. Motivation

Studies demonstrating the need for HPE and electronic packaging for high temperature applications have been drawn since the 1970's. It has been found that, for example, automotive industry, with the electric and the hybrid electric vehicles (HEV), demands less weight and space in the pursuit of lower fuel and/or battery charge consumption. There is a great expectancy for the power inverters to function at elevated temperatures for long periods of time, not to mention the need for devices available at a cost-effective level. Spacecrafts have similar and even higher challenges for HPE, oriented in ever smaller mass and volume components, with high/low temperature operation flexibilities [5]. In the other side, military industry has specific and strict requirements for their tactical electrical power (TEP) with rigorous and severe reliability capabilities under shock and vibration environments, and under extreme temperature and humidity conditions [7].

One inherent, but fundamental aspect of HPE is the heat extraction rate; all cooling alternatives for power equipments diminish their performance as environmental temperature

increases, therefore providing fast heat removal and reducing the need for active cooling are pivotal for the development of HPE [5].

The advent of WBG devices capable of operating reliably at high temperatures has shifted the technological bottleneck from semiconductors science to the electronic package, in particular to the die attach. Thus, it is imperative to develop a packaging technology capable of resisting the same conditions as the WBG devices, and therefore satisfy the demands of the HPE market.



Figure 4. Some of the industrial fields demanding improvements in HPE⁴

The main factor affecting the reliability of electronic packaging is high temperature; in fact failures show an exponential trending respect to time and temperature [7, 14]. Temperature triggers the failure mechanisms associated with the thermal stresses due to the mismatch of the coefficient of thermal expansion (CTE) between the bonding elements; for the case of die attach: between die, substrate, and the bonding material (see Figure 2).

⁴ Credits of images to websites: Terrag Technologies Inc., NASA, mindtouch, SAGA, and Energy.gov

Market is still governed by Si-based electronics and also is limited by their capacities and stability⁵ to 150°C [25]. Each industry has categorized their thermal operations to set the effective point from which their high temperature needs are unsatisfied. In this way, automotive producers estimated their high temperature start point as 170°C, the well logging industry from 200°C, aerospace specialist found 200°C to be high, while some sensor and signal applications for extreme conditions aim operational temperatures above 300°C [14].

These concerns highlight the performance requirements for die attachment, in specific, the need for high temperature stable material to fulfill the durability expectations for power interconnections. The motivation of the current research is to study die attach material and processes to promote future improvements in performance in chip packages for HPE and high temperature electronic applications.

1.4. Justification

Up to this point it has been shown how the incorporation of WBG semiconductors in HPE has enabled high temperature capabilities without the need of active cooling. However, packaging, especially die attachment, is still a major hurdle for product development. Their working conditions will tend to activate a myriad of failures mechanisms by thermal stresses due to the CTE mismatches between the solder (metal-based) and the die (usually ceramic-based) with the substrate.

⁵ The maximum junction temperature ($T_{j,max}$) marks this limit.

Advances in alternative options for lead free die attach solutions for high temperature applications have been found in literature (see section 1.2.2), but there are still also too much blurring technological restrictions that have to be overcome.

Moreover, the complexity of the packaging tasks has been increased by environmental regulations where lead (Pb), traditionally used as part of the solder material, has been banned by RoHS⁶ regulations and some other international organisms. Consequently, engineering designers and scientists coincide in the need to produce adequate, environmentally benign electronic packaging materials and methods [12, 19, 25–27].

Therefore, this project aims at the investigation of a lead free, low energy processing, high temperature stability, and low-complexity solution for die attach for high power and temperature environments.

Silver as a noble metal, with high melting point (961°C), and the highest thermal and electrical conductivities ⁷ [28], is poised to become an excellent option as die attach material. However, if the traditional soldering method of reflow is to be used with silver, it will require a processing temperature close to 1000°C owing to the fact that melting is required to form a solder joint. This elevated temperature is completely out of the range of commercially available equipment and will cause catastrophic damage to the whole assembly, therefore to use silver as a die attach material a new approach must be developed first. This thesis presents the study of a novel and reliable solution that incorporates a material and a methodology, for enhancing the high temperature resistance of a die attach, while using a relatively low processing temperature. This solution uses powder metallurgy methods in the *sintering of silver nanoparticles* to

⁶ Restriction of Hazardous Substances Directive 2002/95/EC, emitted by European Union in February 2003.

⁷ Thermal conductivity 430 W/mK and electrical conductivity 62 MS/m [28].

fabricate a compact material capable of forming a resistant joint. This technique promises very low processing temperatures (relative to maximum operation temperature), low contamination and reaction problems, higher operation temperatures, a melting point close to bulk silver, high conductivity and high heat dissipation capability. As well, sintering has showed to make easier 3-D high-density integration in packaging of HPE, and may reduce the fabrication complexity and costs [12].

Sintering of nanoparticles is a relatively novel technique, born inspired on classical powder metallurgy; it takes advantage of the high energy available in nanoparticles to reduce the external energy injection⁸ during the manufacturing process; instead, nanoparticles provide their free energy to activate a massive diffusion process, which at the end delivers a sound product with properties which promises to be suitable for high temperature die attach applications.

Chapter 2 will present a fundamental discussion on geometry, thermodynamics, kinetic considerations, and behaviors involved in the sintering of nanoparticles, in order to provide the underlying basics of the process. Aside, for competitive and technological back up about the criteria on choosing sintering for alternative solution, chapter 3 will expose a state of the art of the advances achieved in sintered solutions for packaging.

⁸ Traditional sintering metallurgy uses high processing temperature (energy input) plus pressure (external work).

1.5. Objectives

To study the progression and mechanism of low temperature and pressureless sintering of Ag-nanoparticles as an environmentally benign material and process for the functional interconnection of wide bandgap semiconductors.

1.5.1. *Specific Objectives*

- ✓ To determine a medium for the dispersion and handling of Ag-nanostructures prior to the sintering process.
- ✓ To assess the progress of the sintering mechanism by microstructural analysis.
- ✓ To propose the development and evaluate the feasibility of a pressureless sintered nano-silver attach on the basis of the microstructural analysis.
- ✓ To study the effect of the critical factors that control the sintering process in order to advance the development of a high temperature interconnect material.

2. BACKGROUND IN SINTERING OF NANOPARTICLES

This chapter aims to expand the knowledge on the responses of materials when their dimensions are reduced to a point where their behavior as a continuum fuzzes with that of discrete matter. This critical transition will be analytically and physically explained to favor a better understanding of the fundamentals.

2.1. From macro to nanoscale materials

Bulk material's properties are well known and readily available in literature, but in smaller length scales the atomic/molecular effect takes a significant role in determining these properties. This is because bulk (internal) atoms are fully bonded to the adjacent atoms resulting in a stable state, whereas surface atoms are missing bonds, therefore they have an excess internal energy which generates an energetic unbalance [23].

The following topics shows how the size and shape of the particles surface have a direct influence in their energetic state. To illustrate the bulk-to-surface-effect when transitioning from the macro to the nanoscale lets consider a cubic object with a length size of 1 m. If it is divided in small cubes of 1 μm it will result in 10^6 segments by side, which will total 10^{18} segments, where there will be a total of 6×10^{10} surface segments. It is important to note that while the segment's size decreases, the total surface area in the whole segmented body also increases (with respect of that of the original cube) proportionally with the new number of segments; meanwhile, the total volume remains constant. Table 1 presents the quantitative variation of the surface-to-

volume ratio with the change in the size of the segment, and the change in the order of magnitude is evident. Meanwhile, Figure 5 shows a visual perspective of the progression of change in the surface area with respect to the change in size of the segments for the same original cube.

Table 1. Surface to volume ratio grows as the segment size decreases

Segment Size	# of segments in a side	total segment quantity	Surf. area to volume ratio
1 nm	1.0 E+09	1.0 E+27	6.0 E+06
1 μ m	1.0 E+06	1.0 E+18	6.0 E+03
1 mm	1.0 E+03	1.0 E+09	6.0 E+00
10 mm	1.0 E+02	1.0 E+06	6.0 E-01
100 mm	1.0 E+01	1.0 E+03	6.0 E-02
1 m	1.0 E+00	1.0 E+00	6.0 E-03

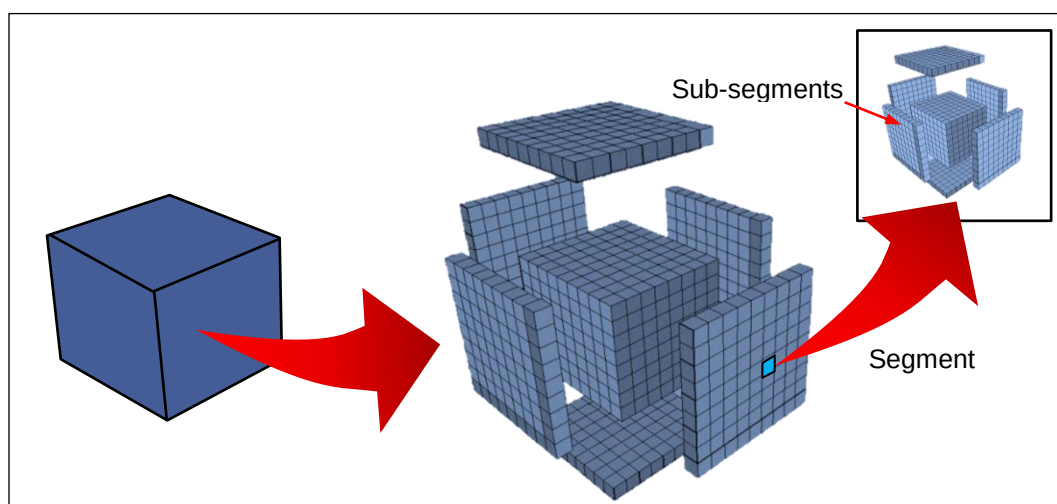


Figure 5. Original surface multiplies geometrically when a body is sequentially divided from segments to sub-segments.

As a particle sets smaller and it approaches to the nanoscale, it transforms from being constituted from a huge number of (bulk) atoms to a group of few ordered and connected atoms (molecules). In these circumstances, when particles get to the nanoscale, the surface atoms are no longer negligible as they are for larger length scales, where the vast amount of bulk atoms

surpasses the number of surface atoms. This gradual change of atom proportions produces an abrupt jump effect when the dimensions go under 100 nm. This pivotal effect has being documented [23, 29]. Figure 6 clearly illustrates the jump effect for the example of the segmented cube.

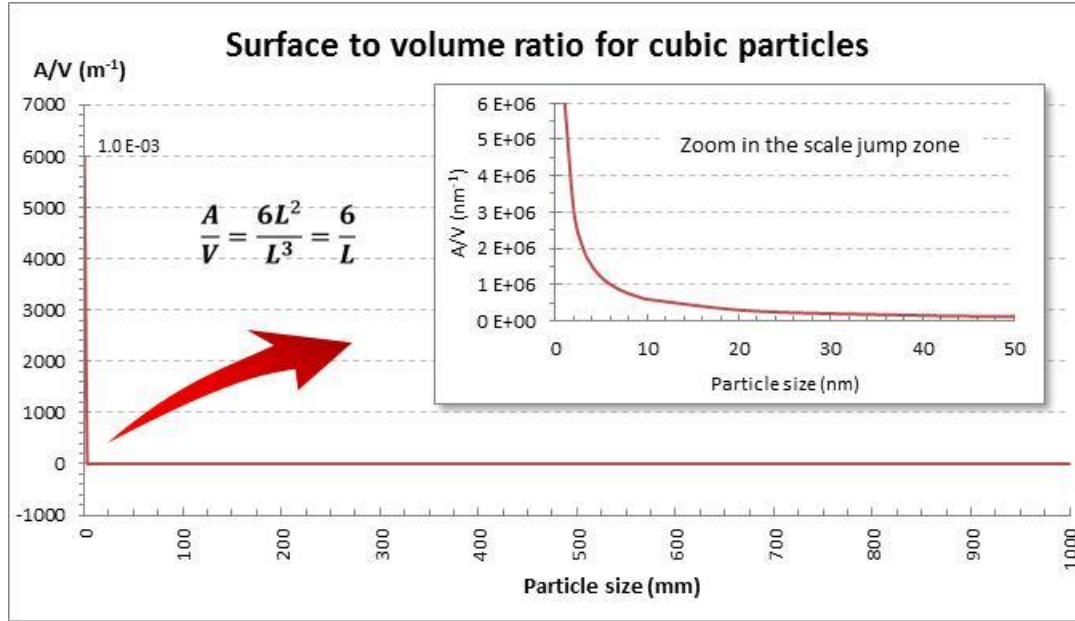


Figure 6. Jump effect produced when the particle size reduces to the scale transition from macro (m) to nanoscale (nm)

On a thermodynamic basis, atoms at the surface have higher internal energy and more freedom to move, which means higher entropy. These two factors are the origin of surface free energy of nanoparticles and of their surface effect [29, 30]. This effect has a pivotal impact in the equilibrium of the materials properties, such electrical, magnetic, optical, and thermal; consequently, nanoparticles possess a natural propensity to agglomerate and to aggregate, i.e. to sinter. Three zones in the thermodynamic system have been defined: the bulk (of solid phase), the surface (the interface) and the vapor phase, where the bond state of atoms at the interface determines the thermodynamic potential, i.e., the propensity to react with the surroundings.

2.2. Fundamentals of sintering

From a thermodynamic perspective, sintering is a bonding process for particle's consolidation into solid shapes using thermal energy and pressure as driving forces. These forces produce a mass transpose phenomenon (atomic movement) and a conforming work, which result in a compact with properties quite comparable with the bulk state of that material. As a continuous system, particles (powders) being sintered behaves with a fluid like character, which powder metallurgy has traditionally exploited for manufacturing purposes [31].

As a manufacturing technique, sintering comprises synthesis, because it produces an in situ different material from the original(s), as well as it is considered a processing method because it allows the manipulation of critical parameters (variables) to obtain controlled properties in the product.

The evolution and the proposed analytical model used to describe the sintering mechanisms are presented next.

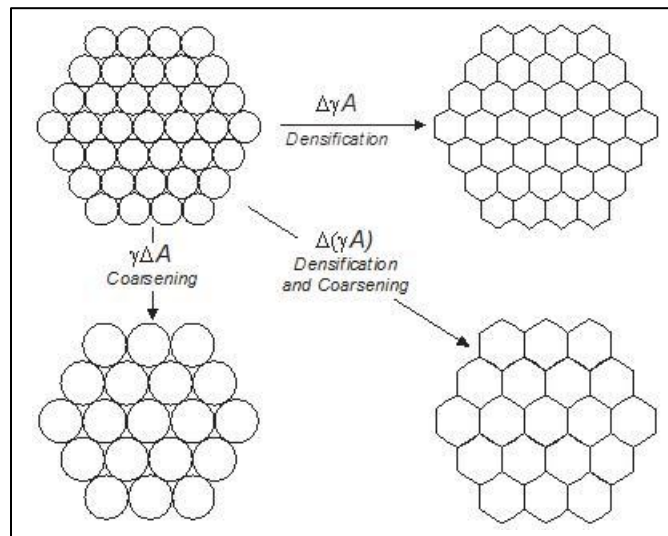


Figure 7. Resulting structures of the basic mass transport mechanisms during sintering [32]

When nanoparticles reach a maximum energy level, a mass transport mechanism starts by reducing their surface free energy; which leads to coarsening/densification phenomenon (see Figure 7). The total reduction in the interfacial energy ($\Delta\gamma A$) can be expressed as shown in equation (1.1) [32].

$$\Delta(\gamma A) = \Delta\gamma A + \gamma \Delta A \quad (1.1)$$

Where γ is the surface free energy and ($\Delta\gamma$) is due to densification and the change in the interfacial area (initial surface area) and (ΔA) is the result of the coarsening effect originated by the mass transport mechanism, as depicted in Figure 7.

Lattice structure and lattice defects (vacancies and distortions) have a significant influence in atoms mobility and in the system instability, thus producing a permanent push to recover the crystalline alignment (which is straight and faceted). Any curvature will compete with the natural crystalline alignment, hence moving the system to a high energetic potential.

2.3. Thermodynamics of the surfaces

It is clear that the surface of a material marks an interface between the bulk and its surroundings. As it was mentioned in the previous sections, surface atoms (interface with surroundings) have different bond state, different distance among them, different mobility and different internal energy. Then to keep going on the energetic analysis it is necessary to clear some physical concepts. Some key concepts for our analysis are presented here:

1. *Interface*. It is the dividing plane existing between different crystals or two different phases.

A surface is a type of interface which is defined as the separation between a condensed phase (solid or liquid) and a vapor phase (or dispersed phase) [32].

2. *Surface energy*. Physically, it is the excess energy of surface atoms with respect to the bulk atoms. In other words, it is the reversible work required to create a unit of surface area at a constant temperature, volume and chemical potential [32].
3. *Free energy*. It is the energetic difference between a small body (under study) and the same number of atoms in a reference crystal (an infinite stable crystal) of the same type [33].
4. *Chemical potential*. It is the change in free energy of the surface associated with transferring one atom from the reference crystal to the body. It is directly related with the increment of the available energy at the surface [34].
5. *Thermodynamic potential*. It represents any energy form available in a system to produce work from it. Physically, it represents an analogy with the mechanical potential energy. There are four basic thermodynamic potentials:

- *Internal energy (E)*: it is the total energy (the sum of kinetic and potential energies) attributed to the particles of matter and their interactions within a system.
- *Enthalpy (H)*: is associated with processes with constant pressure and a work generation through a volume change in the system (defined as $W=P\Delta V$) and by heat exchange with the surroundings. It is defined as

$$H = E + PV \quad (2.1)$$

- *Helmholtz free energy (F)*: represents the reversible work in a system at constant temperature, volume and chemical potential; and it is defined as

$$F = E - TS \quad (2.2)$$

where TS represents the energy obtained from the environment [32, 35].

- *Gibbs free energy (G)*: is the maximum work that can be extracted from a close system at a constant pressure and with heat exchange [35]; and represented by

$$G = E - TS + PV \quad (2.3)$$

Additionally, it brings an inside of the spontaneity of the process.

The phenomenological understanding of the thermodynamic involved in sintering starts with considering a system formed by two homogeneous phases (α and β) in a thermodynamic space, with an interface (σ - associated to α); as depicted in Figure 8.

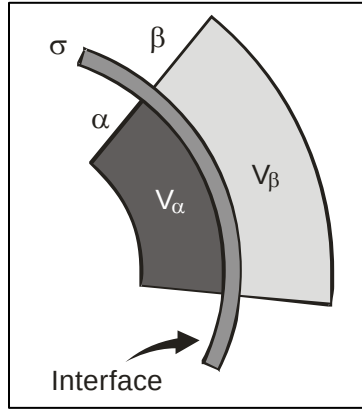


Figure 8. Thermodynamic system of two phases separated by an interface [32]

In a system like this, the thermodynamic potential determined through the Legendre transformation with the Helmholtz and Gibbs potentials [32], is given by:

$$\Omega = F - G \quad (2.4)$$

Where by definition, for this system G changes from

$$\mu_i = \frac{\partial G}{\partial n_i}; \quad \text{to} \quad \mu_i = \frac{G}{n_i}; \quad \text{then} \quad G = \sum_{i=1}^m n_i \mu_i$$

Here μ_i and n_i are the *chemical potential*⁹ and the mole number of the i_{th} element in the system, respectively [32]. It refers to the self-tendency of the substance or phase to chemically react, but also have other implications in the bias of substance to change their aggregation state

⁹ The chemical potential (μ) is thermodynamically defined as
 $\mu_i = \frac{\partial G}{\partial n_i}; \quad \mu_i = \frac{\partial F}{\partial n_i}; \quad \mu_i = \frac{\partial H}{\partial n_i}; \quad \text{or} \quad \mu_i = \frac{\partial E}{\partial n_i}$

or, to migrate to another place [36]. In fact, μ relates with each of the four thermodynamic potentials, but depending on the mechanism of the process.

The thermodynamic potential of the interface is by definition the total surface energy (γA), from equation (2.4) 2.1 it is defined as:

$$\gamma A = F_{\sigma} - \sum_{i=1}^m n_{i\sigma} \mu_i \quad (2.5)$$

From where the surface free energy per unit area is given by

$$\gamma = \frac{F_{\sigma}}{A} - \sum_{i=1}^m \Gamma_{i\sigma} \mu_{i\sigma} \quad (2.6)$$

Here, A is surface area, F_{σ} is the Helmholtz potential, Γ_i is the number of exceeding moles of the i_{th} adsorbed to build a unit area. This expression is applicable when the system holds the same temperature, volume and chemical potential [23, 32].

By definition it was stated that

$$\gamma \equiv \left(\frac{\partial E}{\partial A} \right)_{S, n_i, V_{\sigma}, V_{\beta}} \quad (2.7)$$

Thermodynamically, this formula defines γ as the reversible work to create a unit area of surface, without dissolution, mass or volume change in each phase.

2.4. Mass transport phenomenon due to curved interfaces

This section presents a short derivation of the analytical model for the mass transport driving force in terms of an isothermal phenomenon without chemical reactions and with an only one solid phase. It is also supposed that in this process material transport dominates the overall kinetics of any changes [32].

2.4.1. Surfaces interactions of the two phases

For a system with constant volume (V), as temperature (T) and chemical potential (μ_i) its net change in thermodynamic potential (Ω) is zero [32], as showed below

$$\Omega = \Omega_\alpha + \Omega_\beta + \Omega_\sigma = 0 \quad (2.8)$$

$$\text{or} \quad -P_\alpha V_\alpha - P_\beta V_\beta + \gamma A = 0$$

since $dV=0$, i.e., the net change in α is the same as in β , then,

$$P_\alpha - P_\beta = \gamma \frac{dA}{dV_\alpha} = \gamma K \quad (2.9)$$

Taking K as the average curvature of zones 1 and 2 (see Figure 9), the *LaPlace* [32] equation can be obtained:

$$K = \left(\frac{1}{r_1} + \frac{1}{r_2} \right)$$

$$P_\alpha - P_\beta = \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \gamma \quad (2.10)$$

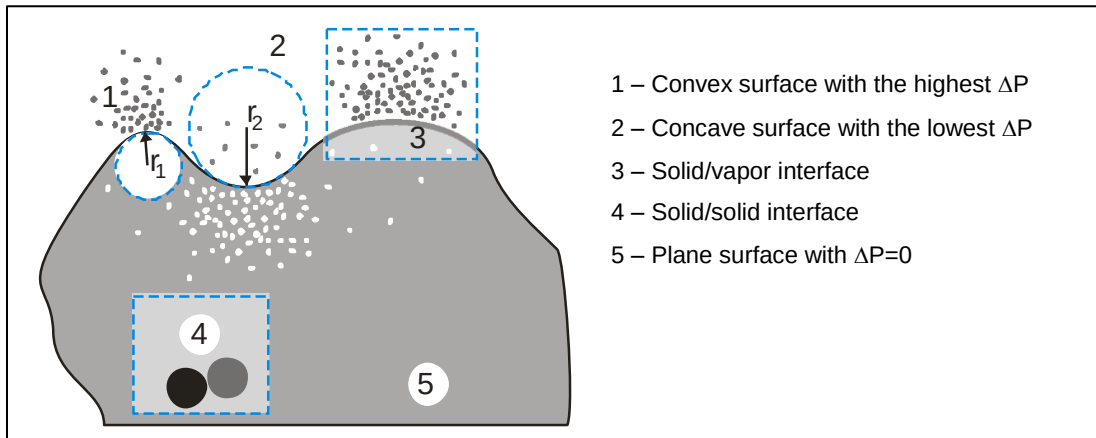


Figure 9. Surface influences in the pressure change

Equation (2.10) describes the thermodynamic potential generated by virtue of two curved surfaces and the pressure changes (see Figure 9). If the body is a small enough sphere then the curvature produces a change in the equation (2.10):

$$P_{\alpha} - P_{\beta} = \frac{2}{r}\gamma \quad (2.11)$$

Under the aforementioned conditions and for the case in which the interface belongs to α phase¹⁰, Gibbs-Thompson equation¹¹ provides a relation between the bulk chemical potential (μ_{∞}) for the two phases and the interfacial energy [32]:

$$\mu_{r\beta} = \mu_{\infty\beta} + \gamma KV_{m\alpha} \quad (2.12)$$

Grouping this equation and re-expressing in terms of the atom activity (a), it changes from

$$\Delta G = \mu_{r\beta} - \mu_{\infty\beta} = \gamma KV_{m\alpha} \quad \text{to} \quad RT \ln \frac{a_r}{a_{\infty}} = \gamma KV_{m\alpha}$$

where R is the ideal gas constant, T is temperature, V_m is molecular volume, the subscript r applies for properties in the curved zone, while the subscript ∞ applies for the bulk conditions [32].

It has been shown that for nanoparticles the atomic mobility gradient between bulk and the surface is $(a_r - a_{\infty})/a_{\infty} \ll 1$ [32], then

$$a_r \cong a_{\infty} \left(1 + \frac{2\gamma V_{m\alpha}}{RT r} \right) \quad (2.13)$$

Equation (2.13) evidences that atom migration promotes because of the curvature and it is higher in convex, rather than in concave curves. This is owing to r is negative in concave curves [23, 32]. (See Figure 9).

2.4.2. Surface interactions of the condensed phase

In equilibrium conditions at constant temperature, when single component system in the condensed phase, due to $d\mu_{\alpha} = d\mu_{\beta}$ for any infinitesimal and reversible change between α and β phases, then

¹⁰ It also means that $\mu_{\infty\beta} = \mu_{r\beta}$

¹¹ Known as well as Thompson-Freundlich equation

$$V_{m\alpha}dP_\alpha = V_{m\beta}dP_\beta \quad \text{and,}$$

then equating, it becomes

$$V_{m\alpha}d(P_\alpha - P_\beta) - (V_{m\beta} - V_{m\alpha})dP_\beta = 0 \quad (2.14)$$

where V_m is the molar volume. Since $P_\alpha - P_\beta = \gamma K$, the integration of equation (2.14) from 0 to K and from P_0 to P_β gives the total reversible work for mass transport [32] and it has been represented as:

$$P_\beta - P_0 = \gamma K \frac{V_{m\alpha}}{(V_{m\beta} - V_{m\alpha})}$$

and similarly for α phase

$$P_\alpha - P_0 = \gamma K \frac{V_{m\beta}}{(V_{m\beta} - V_{m\alpha})}$$

For the case in which β phase is the dispersed phase and applying the ideal gas law [32], the equation can be simplified to:

$$P_\alpha = P_\infty + \frac{2\gamma}{r} \quad (2.15)$$

Similarly with α phase, but considering that $V_{m\alpha} \ll V_{m\beta}$ and P_β as the vapor pressure of α , the result is

$$p_\beta = p_\infty \left(1 + \frac{2\gamma V_{m\alpha}}{RT r} \right) \quad (2.16)$$

By inspection of equation (2.16) a pressure gradient¹² among α and β phases can be defined (similarly to eq. 2.13); but even more, this equation can also be applied to calculate the vacancy concentration gradients in analogous way. Equations (2.15) and (2.16) are probably the most representative expressions of the mass transport phenomena in sintering [32]. They

¹² This gradient is defined when $(p_r - p_\infty)/p_\infty \ll 1$

confirm that pressure gradients are concentrated in convex surfaces and they are inversely proportional to the radius of curvature (r) at the particle surface; hence inducing a local mass transport mechanism in the curved surface. All these gradients are present at the same time and occur in parallel.

In a broader sense, it can be shown that surface energy depends on the crystal structure (planes), on the number of broken bonds in the surface atoms, the energy available for free bonds, and the lattice structure and defects, among many other factors. As consequence, surface energy depends also on the crystal orientation (their homogeneity), as well as the surface shape (because it can interrupt or favor such microstructural order) [23, 34].

As presented, this thermodynamic model of sintering has many assumptions: isothermal, constant chemical potential, material homogeneity, etc. but even though the phenomenon involves too many variables making the analytical modeling¹³ a complex task. Next section shows the application of these equations over the evolution of sintering.

2.5. Sintering progression

Sintering is fundamentally characterized by three stages: *the initial* stage, dominated by the aggregation of particles and distinguished by the formation of *necks* between particles in contact, with a resulting interchange of atoms. A 2 to 3% in volume shrinkage can be observed due to atoms migration through these formations. The second stage is the *intermediate*, where the major densification process is completed via several mass transport mechanisms, it has been reported that a ~93% of the relative density of the bulk material can be attained [32]. The third and *final*

¹³ This model only covers the driving forces of sintering; it does not include kinetics or progression.

stage, is accomplished by a densification process via pore isolation and reduction. Although there are simplified models for each individual stage, the complexity of the phenomenon has just allowed a discrete approach where the validation of the model as a continuous system along the stages is far from being mature. The most known models are the *two-particle model* for the initial stage, the *channel pore model*, for the intermediate stage and the *isolated pore model* for the final stage.

2.5.1. Mass transport mechanisms

There is not a kinetic model to describe the overall sintering process across its three stages. The most commonly used models work with two particles with the same sizes, but there are models that treat the case of particles with different sizes each [32]. In this section the model for particles with the same size will be presented along with the analysis of the sintering mechanisms.

During the necking process, which is the basis for the sintering evolution, there are two accepted mechanisms: necking with shrinkage or without shrinkage, as depicted Figure 10.

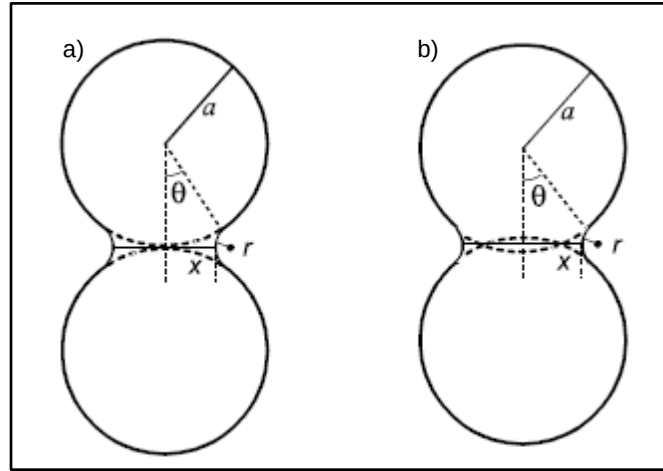


Figure 10. Two-particle model for initial stage sintering without shrinkage (a) and with shrinkage (b). Where a is the particle diameter [32].

The non-shrinking mode does not implies neither a significant change in the distance between particle centers, nor a grain size increase, but they do suppose changes in particle radius (a), neck radius (x), and curvature radius (r); thus this mechanisms do not lead to densification (see Table 2). In the shrinkage mode the overall geometry changes due to the reduction of particle distances, which produces changes in neck diameter, in curvature and at the end it supposed an appreciable change in the particle diameter. By the advance in this mechanism densification makes evident [12, 32]. The sintering stage effectively refers to necking followed by intermediate densification-bridging to finish up with the pure densification, where the porosity of the system is reduced or eliminated.

Table 2. Geometrical evolution of necking during first stage sintering [32]

	Without shrinkage	With shrinkage
Curvature radius	$r \approx \frac{x^2}{2a}$	$r \approx \frac{x^2}{4a}$
Neck area	$A \approx 2\pi x 2r = \frac{2\pi x^3}{a}$	$A \approx \frac{\pi x^3}{a}$
Neck volume	$V \approx \int A dx = \frac{\pi x^4}{2a}$	$V \approx \int (\pi x^2 2r) dx / 2 = \frac{\pi x^4}{4a}$
Observation	Note that without-shrinkage values are two fold of those with-shrinkage.	

Owing to the wettability of particles which also plays a role in necking, it is expected that the r value increases, due to the dihedral angle (ϕ) at the contact point of the two surfaces (especially in the model without shrinkage). Then for ($x/a \ll 1$), then r becomes [32]:

$$r = \frac{x^2}{2a \left[1 - \cos \frac{\phi}{2} \right]} \quad (2.17)$$

For simplification the expression in Table 2 will be used in this work. As shown before, one of the thermodynamic driving forces of sintering is manifested by bulk and vapor pressure gradients; thereby, applying equations (2.15) for the mass transport process from each particle to the neck area using the non-shrinkage model results in

$$\Delta P = P_a - P_r = \gamma \left(\frac{2}{a} + \frac{2}{r} - \frac{1}{x} \right)$$

For ($a \gg x \gg r$) the following equations are obtained from equations 2.15 and 2.16 the driving forces of sintering remain defined as:

Table 3. Driving forces for the two particle model without shrinkage

Gradient	Equation
Bulk pressure	$\Delta P \cong \frac{\gamma_s}{r} \quad (2.18)$
Vapor pressure	$\Delta p = p_\infty \frac{V_m \gamma_s}{RT r} \quad (2.19)$
Vacancy concentration	$\Delta C_v = C_{v,\infty} \frac{V'_m \gamma_s}{RT r} \quad (2.20)$

From here V'_m and V_m are the molar volume of vacancies and of the solid respectively; it has been shown that $V'_m \neq V_m$ by the relaxation of the atoms around vacancies.

Several mechanisms for mass transport occur simultaneously during sintering; the dominant mechanism depends mostly on particles and neck dimension, on temperature, as well as on time.

Table 4 shows the mass transport mechanisms¹⁴ and they are depicted in Figure 11.

Table 4. Mass transport mechanisms during sintering [32]

Material transport mechanism	Material source	Material sink	Related parameter
1. Lattice diffusion	Grain boundary	Neck	Lattice diffusivity, D_l
2. Grain boundary diffusion	Grain boundary	Neck	Grain boundary diffusivity, D_b
3. Viscous flow	Bulk grain	Neck	Viscosity, η
4. Surface diffusion	Grain surface	Neck	Surface diffusivity, D_s
5. Lattice diffusion	Grain surface	Neck	Lattice diffusivity, D_l
6. Gas phase transport			
6.1. Evaporation/ condensation	Grain surface	Neck	Vapor pressure difference, Δp
6.2. Gas diffusion	Grain surface	Neck	Gas diffusivity, D_g

The diffusion equations quantify the amount of material transported by the driving forces; for sintering this quantification refers to atoms and vacancy fluxes [32], as follows:

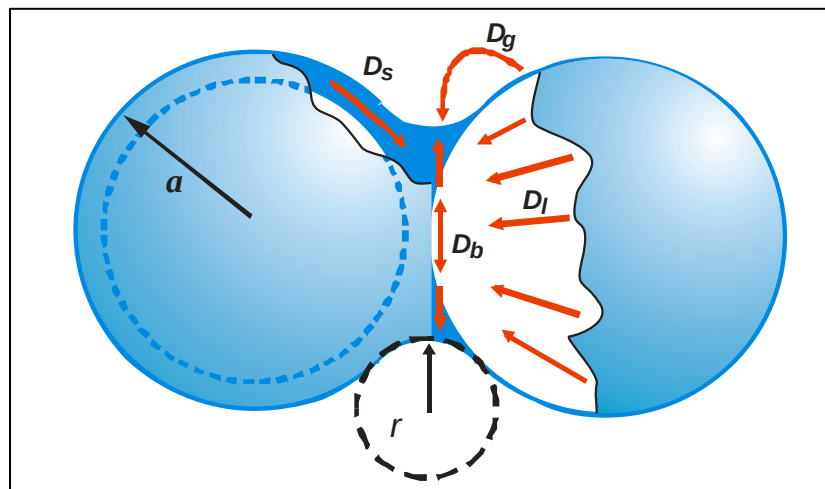


Figure 11. Routes of mass transport during sintering

¹⁴ The analytical models for these mechanisms are given in Appendix VI

$$\text{Atoms flux}^{15}: \quad J_{atom} = -\frac{D_a}{RT} (\Delta P) \frac{1}{L} \quad (2.21)$$

$$\text{Vacancy flux}: \quad J_V = -\frac{D_V C_{v,\infty} V'_m}{RT r} (\Delta P) \frac{1}{L} \quad (2.22)$$

where D_a and D_v are the atom diffusion coefficient and σ the pressure

Kang [32] and Hosokawa [29] presented an extended analysis on the material transport phenomenon in sintering and its kinetics (see Appendix VI).

2.5.2. Effect of sintering variables on sintering kinetics

As the diffusion process progresses during the neck growth stage, the available surface energy in the particles progressively reduces.

The three stages of the sintering process are not sequential, in reality they occur simultaneously. However each of them is dominated by a particular mechanism, thus for simplification of the modeling task each stage will be treated as discrete step with that critical parameter as the main process variable.

The more advances the diffusion process during the neck growing, the more reduces surface energy in particles, and so on. The three stages of sintering do not have a specific time or parameter to start, instead they develops simultaneously; then to reduce the complexity of models, it is important to determine the dominant mechanisms in each stage, and that depends on the variables of the.

¹⁵ L is the diffusion distance or length evaluated for atoms translation.

2.5.2.1. Particle size

For particles having the same morphology but different sizes, the *Herring's scaling law* predicts the instant when they both get the same degree of sintering [32]. Two spherical particles with radii a_1 and a_2 , where $a_2 = \lambda a_1$, the required sintering times t_1 and t_2 are related as follows

$$t_2 = (\lambda)^\alpha t_1 \quad (2.23)$$

Using the definition of atomic flux

$$t = \frac{V}{JAV_m} \quad (2.24) \quad \therefore \text{ where } V \text{ is volume,}$$

to replace in diffusion equation (2.23), the solution for this system can be satisfied and approximated to $\sim L^3$, where $L^3 \sim \lambda^3$, meaning that $\alpha=3$ for lattice diffusion [32]. Using equations (2.24) and (2.23) the equation for sintering kinetic of particles with different sizes can be expressed as:

$$\left(\frac{x}{a}\right)^n = F(T) a^{m-n} \cdot t \quad (2.25) \quad \therefore \text{ where } F(T) \text{ is a function of temperature,}$$

x is the neck radius, and a is the particle radius

Perhaps this equation does not describe the grain growth kinetic, it is quite valid and it applies on the basis that particles evolve through the same sintering mechanism.

2.5.2.2. Temperature

Okuyama [37] presented an expression derived from the surface area¹⁶ rate of change:

$$\frac{dA}{dt} = \frac{1}{\tau} (A - A_f)$$

to provide an expression relating the final neck radius (l), the initial and final particle radii, with temperature (T). It is a two state equation as presented here:

¹⁶ A_f = surface area of the final sphere after complete aggregation,.

$$\tau = A_{\tau}(2a_f)^m \exp\left(\frac{E}{RT}\right) \quad (2.26)$$

$$A_{\tau} = \frac{kT(2l/a)^6}{12bD_0\gamma_s V_m}$$

In these equations l corresponds the neck radius when it gets the 83% of the particle radius in any moment (a_f), while a are the final and initial particle radius; τ is called the *sintering time* and is a rate constant, γ_s is the surface energy, k is the Boltzmann constant, D_0 is the diffusion coefficient, V_m is the atomic volume, E is the activation energy and R is the ideal gas constant. In equation (2.27), A_{τ} is constant and depends on the sintering mechanism¹⁷.

Equation (2.28) shows that neck growth and shrinking rate are in exponential function of temperature with respect to temperature [32]. Therefore, it is evident that progression is very sensitive to processing temperature.

Other variable into take into account in sintering is the chemical composition, which can be exploited by increasing vacancy concentration or choosing a material with appropriate diffusivity [32].

2.5.3. Intermediate stage model

The most widely used model for this stage has been presented by Coble [32]. This model simulates the evolution of the already aggregated particles which form tetrakaidecahedral grains connected in a highly porous structure. These pores are located in the remaining cylindrical-shaped space between particles, i.e., along each grain edge (see Figure 12) [32].

¹⁷ The expression showed of A_{τ} corresponds in this case to grain boundary diffusion.

Grains in Figure 12 have 14 faces, therefore this stage develops mainly by lattice diffusion and grain boundary diffusion. The following equation presents the lattice diffusion, which is responsible for the rate of relative density (ρ) variation [32].

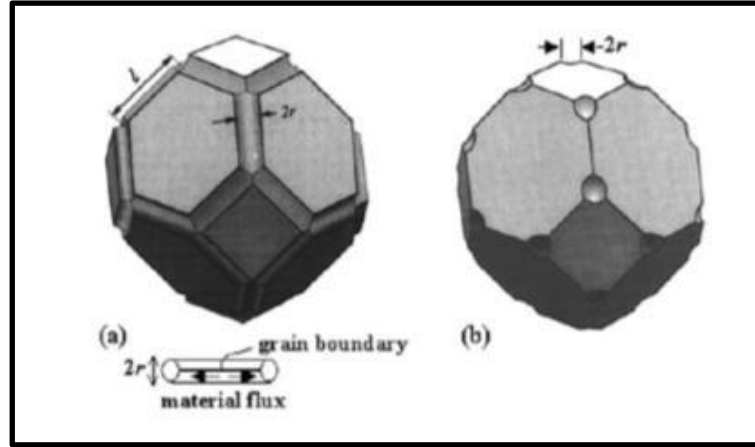


Figure 12. Grain formation according to Coble's model [32].

$$\frac{d\rho}{dt} = \frac{336D_l\gamma_s V_m}{RTG^3} \quad (2.27)$$

where G is the grain diameter which fulfills the geometrical relation

$$\left(\frac{\pi}{6}\right) G^3 = 8\sqrt{2} \cdot l_g^3$$

The following equation shows how the grain growth influences the densification process through the boundary diffusion mechanism [32]

$$\frac{d\rho}{dt} = \frac{854D_b\delta_b\gamma_s V_m}{RTG^4} \left(\frac{1}{P_v}\right)^{\frac{1}{2}} \quad (2.28)$$

2.5.4. Final stage model

This stage is dominated by pore isolation and shrinking, where the pores are represented as spherical voids on each vertex of the growing tetrakaidecahedral grains, as illustrated in Figure 12b (with the yellow core). The model suppose concentric spherical gradient of atoms diffusion

The densification rate of this model is given by the equation

$$\frac{d\rho}{dt} = \frac{288D_l\gamma_s V_m}{RTG^3} \quad (2.29)$$

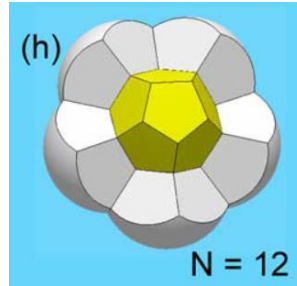


Figure 13 . A close pore representation [47]

2.5.5. Discussion

This review on the analytical models of sintering showed the tools that describe from the state-by-state analysis of discrete particles through the sintering process, along with their kinetic progression through the time. Each model has several restrictions such as thermodynamics, geometrics, atomistic, physics, etc. for the simplification of the up-to-date piecewise knowledge of the involved diffusion phenomena. Provided numerical-analysis-solutions of the proposed models are a useful support, but even their resources result too limited when this analysis are tried to be scaled from the discrete to the continuous approach, as it is needed for real applications, such lead-free bonding. Then, there is not yet a model that gathers the analytical representation with numerical solutions in a strong, consistent, but simple evaluation or prediction tool of the sintering phenomenon towards macro scale bodies conforming.

Since the approach of this study is aiming an inside of the diffusion phenomenon to propose future improving in the sintering process for further solution of die attach, these models constitute just a frame work but the path continuous leading to laboratory examinations. Next chapters provide the experimental development carried along this research.

3. LEAD-FREE DIE ATTACH SOLUTION FOR HIGH POWER AND HIGH TEMPERATURE ELECTRONICS

3.1. Alternatives to lead free die attach technologies

One of the pioneers working on solving die attach problems for high temperature and power electronics was Schwarzbauer [38], who suggested for the first time the *low temperature joining technique (LTJT)* for large area dies. His approach was based on solid state sintering of silver micro-sized flake powder under a constant load of 40 MPa and a temperature of 250°C. The resulting sintered material exhibited a porous structure with acceptable thermal and electrical conductivity together with a melting temperature close to that of bulk silver (961°C). However, the pressure exerted to the SiC devices resulted in severe cracking [38, 39], therefore this technique was ruled out as an effective solution.

Amro [25] reviewed that the favorable behavior of solder alloyings is mainly driven by the formation of the intermetallics phases, however they tend to promote crack initiation at the edges of the joints; these cracks are a niche for shear stress concentration due to the rapid coarsening of particles during sintering. Cracks will propagate through the brittle intermetallics, hence deteriorating the heat dissipation ability of the joint, as well as the material integrity. For this reason, Amro proposed a possible solution to this problem by the implementation of the already documented LTJT in his work. Sub-micron silver flakes, as die attach, were processed, sintered, and subjected to power cycling at $\Delta T_j = 170\text{K}$ ($T_{j,\text{max}} = 200^\circ\text{C}$). From these tests it was reported the aforementioned die attach material survived up to 20,000 power cycles. However, this technique

presented some limitations induced by an increase of the thermal resistance due to aging of the substrate.

There are still questions on how to reduce the detrimental effects of the residual stresses induced by the high processing temperatures. It is also pivotal to get a chemically and mechanically stable material that could work reliable over prolonged period of times subjected to harsh environments, specifically in high temperatures and high power conditions.

From a manufacturing as well as a reliability perspective it is desired to lower the processing temperature of the die attach process. It is also wanted to minimize the usage of highly activated fluxes mainly due to harmful residues. Another important issue that must be taken into account is the formation of thick, brittle intermetallic compounds that are known to affect the durability of the joints, therefore a monometallic system could be a great advantage.

Additionally, it would be quite advantageous to use the thermal energy dissipated during operation, for the continuous improvement of the bonding interconnection; rather than seeing this energy as a trigger for activating a failure mechanism within the system.

Investigations with nanoscale powders have shown that minimal energy, when compared to conventional sintering, is needed for sintering at this scale. It has been theorized that this is possible because at this scale nanoparticles have more surface energy, and thus its total free energy increases. This would make possible to reduce the processing temperature of the die attach fabrication, if an attach material constituted of nanoparticle is obtained. Nano-sized are poised to provide good results even without external pressure, which may yield in the formation of a porous Ag structure with melting point near that of bulk silver. In other words, this can provide a material that can be processed at a relatively low temperature but that can withstand

high temperatures without melting, thus becoming a key enabler for the realization of WBG devices [39–41].

3.2. Sintering approaches with Ag-nanoparticles

Sintering of nanoparticles has been investigated, but further research is still needed for the development of this technique as an alternative manufacturing process. Quintero [11] presented a method for suspending nanoparticles in a medium to form a paste, which was later subjected to an isothermal pre-heat for particle drying and activation, followed by an isothermal treatment at 300°C to achieve coagulation. Published results [42–45] have provided valuable information for further research investigations.

Pressureless coagulation of spherical nanoparticles has been investigated, however a continuous film and consolidation has not been completely attained as described by several researchers [42, 46]. Our hypothesis for this sintering progress limitation resides on the diffusion process and the resulting balancing of free energy. As particles coalesce the unbalance between surface and volume free energy reduces, thus minimizing the driving force for the spontaneous reaction. In other words, particles grow by a necking mechanism where atoms migrate from convex surfaces to concave surfaces until a specific size and shape is reached. It is of utmost importance to understand the sintering mechanism at this length scale to develop empirical and numerical methods that can eventually serve as prediction tools for this proposed manufacturing process.

There is a very wide range of analytical models that can be considered to explain the governing mechanism behind the sintering process. A review of the literature can show the myriad of conditions and configurations that can be considered. As an example, the two particles with the same

shape and size which have already been discussed [12] (see section 0), whereas two particles with different sizes (see section 0), and an aggregate of particles forming a close cell structure have been published respectively [12, 47]. All of them assume the structure and configuration repeats uniformly on a long range order. Each available model deals with very specific geometrical arguments and boundary conditions for its solution. Table 1 enlists several sintering models available in the open literature.

Several authors [12, 29, 32, 48] have presented equations for neck formation and growth on the basis of a controlled diffusion mechanism as function of time and surface area. They explain the driving forces from a mass transport perspective, where the chemical potential gradients (which are affected by the surface curvature changes [12, 48]) and the local stress at the interparticle contacts influence the partial vapor pressure on particle surface [12, 32]; thus generating atom migration to decrease the potential gradients. Qi et al. [49] explained the driving force in terms of the cohesive energy between particles, and demonstrated the particle size effect using Herring's scaling law. This was the base to study the sintering progress in particles of different sizes with the same conditions [32].

Several factors and parameters have been suggested as critical for modeling the sintering mechanism, where the complexity of the task becomes apparent by inspection. The need for simple models to facilitate this task is urgent if the development of sintering as a conventional manufacturing process, is the general concern.

Classical powder metallurgy theory uses these models to calculate the densification rate for diffusion-controlled mechanism together with the thermodynamic driving force (or sintering potential) and an externally applied pressure. Other parameters such as grain boundary energy, surface energy, grain size, and the pore radius (considers a close pore) [12, 39] have been

incorporated into these models. Furthermore, these models have allowed introducing a new two step-sintering method to restrict grain growth by means of controlling the sintering path [29].

Although ambitious models for this multi-stage sintering process exists [50], the computing power required and the processing time makes them impractical for the practitioner where real time and fastest solutions are needed.

Present work will focus on experimental data for the progression of the sintering mechanism in order to assess and present a simplified method built upon the existing models. This will enable the development of the proposed low temperature pressureless sintering of Ag nanostructures as a die attach alternative.

4. LITERATURE REVIEW: SINTERING OF Ag-NANOPARTICLES

Sintering of nanoparticles is driven by their own available free energy which may result in a densely packed structure depending on the evolutionary stage of the process. This chapter describes the sintering process of Ag-nanoparticles together with the main factors that affect and control its evolution.

Many existing complications associated with the practice of sintering nanopowders must be considered when its results are evaluated during a study; such complications may include homogeneity on the particle size, composition, particle distribution, homogeneity in the temperature gradients, among other complications.

There are two main mechanisms for the transformation of the microstructure during sintering, these are densification and coarsening. These two mechanisms are not independent of each other; however they tend to dominate over each other depending on the processing conditions. The non-densifying diffusion has been observed to be dominant at low temperatures, while the densifying diffusion has been observed at high temperatures ranges [12]. The non-densifying sintering process is controlled by surface diffusion, this results in the formation of necks between particles with little densification at relatively low temperatures, thus producing a network-like structure formed by interconnected particles. In the other hand, densification processes are mostly driven by lattice diffusion mechanisms (grain boundary and grain surface diffusion) as depicted in Figure 14 (see also Figure 11).

The concept of high temperature, in terms of sintering evolution, for one material depends on its particle size; for instance, Guofeng [12] reported well densified sintering of silver nanoparticles at 280°C, whereas for the micro-particle paste (commercial¹⁸), a similar densification required temperatures above 500°C.

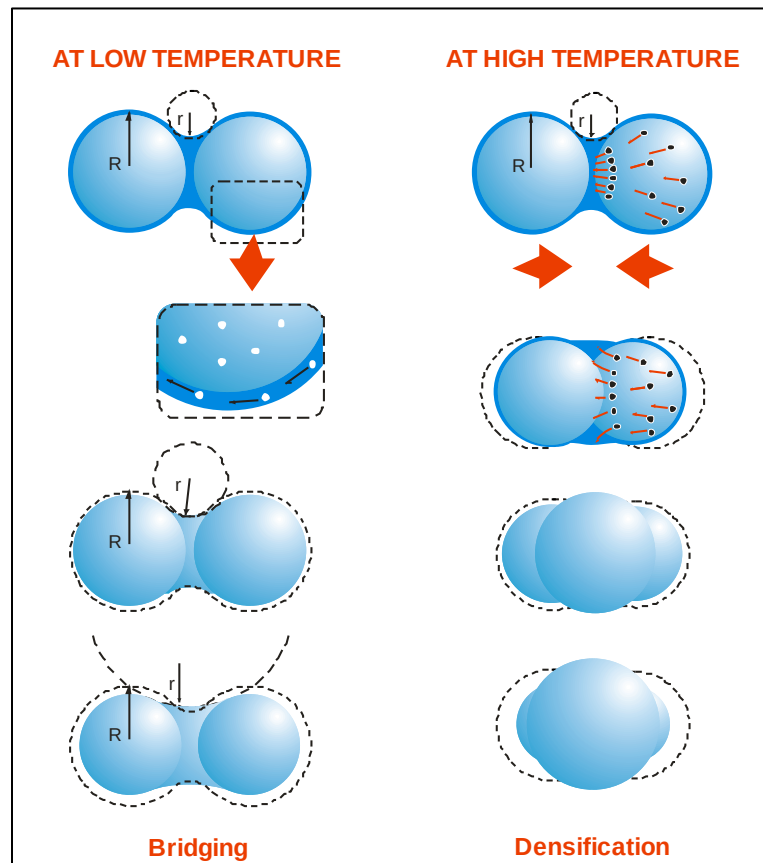


Figure 14. Temperature effect on sintering mechanisms

Research on sintering of silver nanoparticles has been predominantly conducted for low temperature and low power applications [44, 45, 51–53]. The advancements in high power and high temperature electronics had resulted in a tougher mission compared to low power applications, owing to the necessity of obtaining an appropriate material which could resist

¹⁸ Appendix VII presents some properties of commercial pastes.

higher stresses, with thermal stability at higher operating conditions which could yield the demanded performance and reliability.

The following section will be dedicated to present the current advances in material solutions for high power and high temperature die attach.

4.1. Nanoparticles as raw material

Silver nanoparticles can be procured uncapped or coated with organic shells or capping agents. Uncapped particles are susceptible to self-aggregation, contamination and oxidation, however they can be sintered more easily owing to the fact that the surfaces are readily accessible for diffusion. On the other hand, coated particles require a chemical or thermal treatment for organic shell elimination in order to allow the sintering process; but they are less prone to premature sinter and the unwanted non-densifying sintering. It has been shown that nanoparticles tend to keep their initial microstructure until the organic coating is removed to initiate sintering [12]. The size of the nanoparticles is pivotal for the low temperature sintering process, therefore as the desired size keeps decreasing the more critical the use of a surfactant becomes; since its effect on preventing self-aggregation of the particles prior to the activation of sintering mechanism.

As discussed before, the particle size effect on the sintering potentiates the low temperature process. Studies using Ag metallorganic nanoparticles (11 nm) and “fine particles” (100 nm) as joining elements, have been published where the size effect on the bondability to copper has been presented [43] showing superior results with the nano-sized particles.

Next sections will show recent results discussing the processing and handling, sintering, and performance of nanoparticles.

4.2. Silver nanoparticles pastes

Sintering has similarities with the reflow processes, starting with the need for the formulation of a paste, the expected joint formation, and the multiple affections associated with contamination, oxidation, and intermetallic formation, to mention but a few.

Nanoparticles may need fluxes as in commercial pastes, which are constituted of microparticles suspended in a flux medium. The colloidal suspensions might bring oxidation protection, dispersing and binding effects, and they can also ease the rheological performance, and improve the wettability.

All these agents form a complex medium which is (usually) implemented with the addition of organic compounds. There are significant drawbacks to this process such as its effect on the limitation of the metal content in the mixture, formation of gases which may cause contamination, voids, blowholes or the corrosiveness of its residues. Any of these issues may be disturbing to the joint integrity as well as its long term reliability. Fluxes have to be formulated in such way that its rheological agents are conserved up to a specific temperature while its activators may react at a temperature just below the joint formation temperature; this has been demonstrated to be a very difficult task to accomplish [21, 54]. The synthesis or the dispersion of silver nanoparticles are not trivial tasks, there are a significant amount of reagents/methods for synthesis as well as for dispersing and handling, however their performance is still under evolution.

Recent works on sintering of Ag nanoparticles have been focused in pastes or solutions with low metal concentration, which is useful for inks and printed circuit traces aimed for low current applications. Die attach for HPE and high temperature electronics require high metal loads [19, 25, 55, 56] so that after sintering, a dense metallic structure that can handle high currents and the high thermal stresses is attained.

In general, capping agents for dispersion of silver nanoparticles may include polymers, glycols, thiols, amines, and carboxylates, among others; which require high temperatures for its removal [57]. Guofeng [12] suggested fatty acids, fish oil poly (diallyldimethylammonium chloride) (PDDA), poly(acrylic acid) (PAA), and polystyrene sulfonate (PSS), as possible dispersants, while Maruyama [57] chose Alkoxide silver nanoparticles passivation which are easier to remove. Wakuda [45] reported a very stable and low percent capping (2.1 wt.%) of alkylamine.

Additionally, Guofeng [12] also proposed the use of binder agents such as RV 914, polyvinyl alcohol (PVA), polyvinyl butyral (PVB), and wax for retaining nanoparticles together up to the moment of the sintering. For rheological purposes Guofeng also proposed the use of thinners such as Heraeus HVS 100, Heraeus RV 372, Heraeus RV 507, Heraeus RV 912, Texanol, and Terpeneol.

The integrity of the paste has been guaranteed by storage in a close, refrigerated jar (at 5°C) [12, 45, 58]. Wakuda [45] found nanoparticles' grain tend to grow from an initial 15.9 to 21.9 nm when preserved for a month, however they grew to 33.1nm after 48 h when exposed to ambient air.

A narrow size distribution of nanoparticles is difficult to obtain and to repeat during synthesis; nonetheless it provides more confidence in the expected sintering results and a better

correlation to the process variables. Alarifi [58] got a silver nanoparticle paste from an as synthesized solution, with average size of 50 nm with a range going from 20 to 100 nm. Maruyama [57] published results with particles as small as ~5nm, however they also recognized that more than 50% of the sample weight was constituted by large aggregated particles due to the unavoidable aggregation with high concentrated solutions. This self-aggregation is an unavoidable effect typical for all kind of nanoparticles which will be covered in the results and discussion chapter.

There are two main aspects when working with solution handling: storing and deposition. Storing must guarantee the integrity of the system by avoiding excessive evaporation, therefore temperature storage below 5°C is recommended [12, 45, 58]. The paste deposition should be done in such way that avoids excessive material evaporation so that it does not affects the rheology of the paste, hence the final results. The most commonly used methods for deposition are screen printing, syringe deposition, and inkjet printing [12, 58, 59].

4.3. Parameters of the sintering process

Sintering of nanoparticles has been investigated from very low temperatures, as room temperature, 50, 100 and 150°C, [12] to temperatures as high as 200, 250, 300, and up to 500°C [12], along with dwell times from 5 minutes to 24 hours. Environments have been controlled between open air, vacuum, and in inert gas (Ar or N) [12]. The prevalent sintering temperatures for high temperature applications oscillate from 150 to 350°C, and the holding time has been proposed to be between 30 and 90 minutes [12]. As an example, Quintero [60] sintered silver nanoparticles at 300°C, and Guofeng [12] obtained good results at 280°C, however they both

found reliability limitations. Evaluating both cases, and the evidence from other reviewed investigations, it was considered that a temperature of 300°C is an ideal and low enough target in order to enhance the actual advances and to improve the performance of these sintered materials.

In the other side, moving the actual working capabilities of the die attach joints from temperatures below 200°C (as it is normal in the industry), to the projected objective of 300°C, is a great technological jump.

A high heating rate has been suggested [12] during pre-heat stage of the process to prevent the activation of the non-densifying mechanism as discussed at the beginning of this chapter. Afterwards, when ramping to the sintering temperature a thermal spike may be wanted to obtain a well densified structure, however this steep heating rate could cause problems with the rapid evaporation of volatiles which can result in cracks or voids. Hence, the thermal profile as well as the holding temperature becomes critical for processing.

The atmosphere for the process is very important too, for instance, the open air environment (or oxygen enriched) demonstrated to be helpful for the organic burnout during sintering, thus aiding with the effective removal of particle's coating by gasification. It is suggested that the oxygen helps to break the hydrocarbon chains during the organic component burnout easing the elimination of the shell. It has been gotten for the same nanoparticles pastes densification after sintering at 280° in air, while they did not at 350°C in vacuum [12] . Contrary to that, some results have shown that the alkoxide coating disappears in air at 300°C, whereas the same effect has been reported at 200°C in nitrogen atmosphere [57].

The metal load constitutes a very important variable for the sintering results. Commercially available solder pastes have up to 90% metal load by weight, there have been reports showing good results with silver nanoparticle pastes containing up to 85 wt.% metal [12, 43, 60]. Higher

flux contents makes its removal more difficult during sintering; whereas high metal concentrations ease it, but it difficulties the paste deposition [12]. Maruyama [57] mixed 2.5 nm with 400 nm particles sizes to increase the silver content to 89% and to improve densification, using external pressure. Ide [43] showed superior densification with Ag metallo-organic nanoparticles (11nm) when compared to fine particles (100 nm) sintered under pressure. Their results showed no voids or gaps in the interface between Cu and the Ag sintered layer joints.

Some researchers use pressure combined with low temperature sintering to guarantee a full densification of the joint. They have reported different performances [42, 43] with pressures varying from 1 to 5 MPa, and constantly applied throughout the whole sintering treatment,. Alarifi's [58] nanoparticles were fully densified when treated over 200°C for 30 minutes. The thermal analysis have shown that there are several reactions which may occur during the pre-heat stage (<100°C) such as minor organic burning and evaporation. Solvent evaporation (under 200°C [43]) opens the path to flux burn out, which is promptly followed by the diffusion process of the nanoparticles' atoms. First and second reactions are endothermic, whereas the third is an oxidation process (if it is made in oxygen environment) which is exothermic [41, 57].

From thermal behavior analysis it has been found that some nanoparticles pastes joints did not sinter at 350°C in vacuum, whereas they did at 280° in air. The barrier effect of the coating layer (dispersant) for sintering progression stops as it burns, which is usually reached by an oxidation reaction [12]. Other tests in sintering have showed an evolved intermediate stage, which proved to get transformed to the final stage of sintering after thermal aging for months; which evidence the thermal stability of sintered microstructures.

4.4. Performance of silver sintered materials

The reliability of joints has been related with thermo-mechanical stresses generated by the CTE mismatch of the elements that compose the interconnection: die, interconnect material and substrate. The performance of SiC WBG devices has been studied on Al₂O₃ direct bonded copper (DBC) or AlN DBC substrates. These substrates have been metallized with nickel, silver or gold for chemical passivation and to favor the interface interdiffusion [12, 60].

Some studies have shown an elastic modulus for silver sintered materials of 43MPa, which is low when compared to bulk silver, and even lower than that of the commercial pastes. These low values have been attributed to the porosity of the material. A finite element analysis suggested that the sintered silver would transfer less stress to the device (the die) than the gold-tin solder at the same temperature swings, in a die attach joint. This has been explained by the fact that the porosity makes it more compliant even though CTE of silver is higher than that of gold-tin [12].

Alarifi [58] applied sintering to a wiring process where samples were fabricated at 250° and 300°C under 5 MPa of pressure during 30 minutes. The shear strengths of these samples were of 27 MPa and 36 MPa, respectively. Hirose [42] reported 60 MPa of shear strength in a joint¹⁹ made at 250°C for 5 minutes and pressure of 5 MPa. Maruyama [57] obtained, with sintered samples at 1 MPa, shear strength values 1.5 times higher than those of standard soldered joints. Sintering process effectively depends on the size of the precursor particles, however from the practical observations of Maruyama on the inherent self-aggregation tendency of nanopowders it can be seen that a critical control on monodispersion may not be needed.

¹⁹ The Cu/Ni/Au-to- Cu/Ni/Au joint was made with in situ Ag nanoparticles from Ag₂O.

The electrical performance of sintered nanoparticles have been also investigated, Wakuda [45] sintered nanoparticles at 50, 100, and 150°C for 0.5, 1, and 2 hours respectively, and measured their resistivities. For 0.5 hour at 150°C he reported a resistivity of $3.2 \times 10^{-7} \Omega\text{m}$, for the treatment at 50°C after 2 hours, a resistivity $1.1 \times 10^{-6} \Omega\text{m}$ was reported; for non-thermally treated material he reported a resistivity of $4.9 \times 10^{-6} \Omega\text{m}$, which is still low when compared with that of bulk silver ($1.59 \times 10^{-8} \Omega\text{m}$). Electrical and thermal conductivities of the silver sintered materials have been reported to be 3-5 times higher than those of commercial solders [12].

Appendix VII presents a summary of some properties of silver sintered materials compared with those of commercial solders [12].

4.5. Sintering approach of silver nanoparticles

The aforementioned review confirms the potential of sintering of silver nanoparticles as a lead-free solution for die attach. The actual processing temperatures, ranging from 250 to 350°C are low enough; the reported shear strengths of up to 40 MPa with pressure-less joints, and all the benefits obtained for the elimination of interdiffusion issues makes sintering of nanoparticles a very interesting candidate that deserves further research.

There are two relevant factors to consider in the understanding of the involved transformations and the final results in sintering; the first is given by correlating the products of the process with the size of its precursor particles. The second one is to recognize and control the participation of the capping and dispersant agents in such transformations, along with their elimination throughout the process. They both will help identifying the effect of critical

controlling parameters such as temperature, time, and atmosphere in the process. Thus, a better understanding of the sintering transformations will allow the improvement of the process.

The simplicity of the preparation of the nanoparticles will be determined by the composition of the medium and the capping nature; therefore an important factor to consider is the formulation of the system. That is why the experimental work of this research is guided to only one metallic phase (silver) and with the use of simple formulation dispersants, instead of fluxes. Future achievements in sintering may be oriented in the usage of several precursor materials and more complex dispersants.

5. EXPERIMENTAL WORK

The previously discussed theoretical background and the reviews on sintering of Ag nanoparticles were useful for defining an experimental strategy during this investigation. Factors such as temperature, time, atmosphere, material, medium, and size were taken into account for an exploratory study to later formulate a more focused approach.

This chapter presents the different tests developed to further understand the sintering of Ag nanoparticles as a candidate for HPE and high temperature die attach. First, information of materials and equipments used in the present research is presented, followed by the description of the processes and procedures related with material handling and particle processing. Next, characterization tests developed for microstructural analysis, X-ray diffraction, and electron microscopy along with thermal analysis of the raw material, pastes and sintered samples will be discussed.

5.1. Precursor material and management

Three types of silver nanoparticles were used as supplied by Nanostructured & Amorphous Materials, Inc. to drive the studies:

- * Spherical shaped particles, 99.9%, with oleic acid coating with nominal size 30-50 nm, 5-10 m²/g, CAS # 7440-22-4, stock # 0477YDC.

- * Spherical-shaped particles: uncoated, with nominal diameter of ~ 35 nm, 99.5% purity, 30-50 m^2/g SSA, CAS # 7440-22-4, stock # 0476JY²⁰.
- * Flake-like particles: uncoated, 99.5%, ~ 3 m^2/g , 20-80 nm thickness, 0.6-1.2 μm in the plane, CAS # 7440-22-4, stock # 0478YD1.

The previously mentioned necessity and drawbacks of a medium for dispersion of the particles (see section 1.2.2) were considered to develop a dispersant media based on ethanol, propanol, and oleic acid. They were handled in cold temperatures and served (below 5°C) to prevent solvent evaporation.

5.2. Paste preparation and handling

Mixing nanoparticle powders with simple solvents just for deposition purposes eases the particle deposition. A solvent less viscous, less sticky and easy to remove reduces the losses and their controls during the task, although they can bring less protective effects to the particles against the aggregation. The balance of particle's protection and process simplicity was considered to get a simpler dispersant medium.

The pastes were prepared for deposition into the carriers and sample fabrication. Two types of carriers for samples fabrication were implemented: the boat-type carrier (stainless steel sheet) and plate-type carriers (galvanized steel sheet wrapped with aluminum foil) as depicted in Figure 15.

²⁰ Where SSA is specific surface area and CAS is the Chemical abstract service.

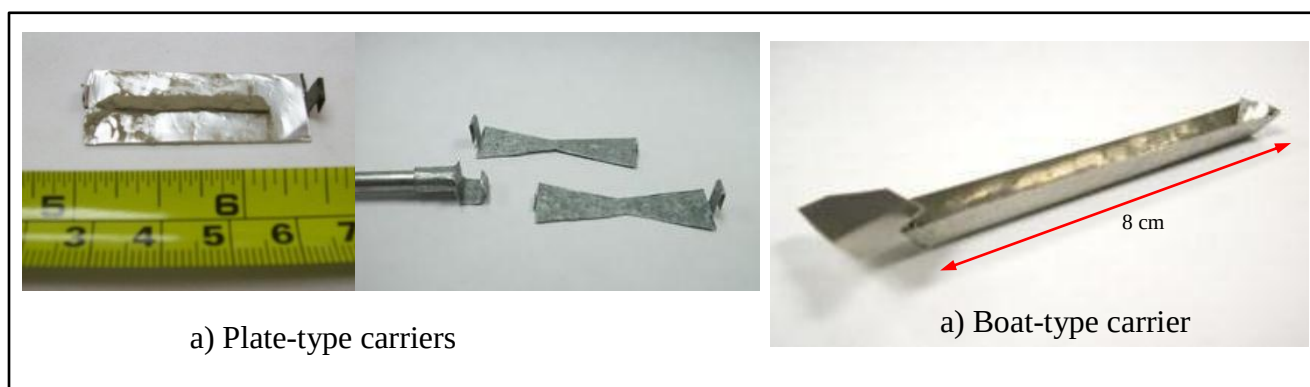


Figure 15. Carriers for sample deposition and fabrication

A procedure for solution preparation, for each type of particle, was designed in order to get an acceptable consistency and stability for paste handling. These procedures are presented as follow:

* *Spherical/uncoated particles (SUC):*

7.5 g of Ag nanoparticles were mixed with 20 ml of ethanol. The ethanol was kept at 5°C before mixing, and once mixed, the solution was kept at 15 °C until the sintering process. The paste was sonicated for powder deagglomeration (i.e. particle dispersion) using 8 cycles, each consisting of 5 minutes hold and 10 minutes still. This sonication procedure will be identified as (5min/10min×8) in the upcoming text.

* *Flake shaped/uncoated (FUC) particles:*

7.5 g of FUC nanoparticles were mixed with 20 ml of 2-propanol. The solution was kept at 15 °C until the sintering process. The paste was sonicated using the 5min/10min×8 procedure.

* *Spherical/oleic acid coated (SOC) particles:*

7.5g of SOC nanoparticles particles were mixed with 20 ml of 2-propanol. The paste was sonicated using the 1min/1min×3 procedure. The solution was always kept at 15 °C until the sintering process.

After preparation, all pastes were stored at 5°C in hermetically sealed glass flasks. Sample preparation is described below:

* *Spherical/uncoated particles (SUC):*

Droplet depositions of 0.03 g of the Ag paste were applied into a plate carrier and dried for 1 minute. All samples were dried at room temperature (22°C) and 70% relative humidity (RH).

* *Flake shaped/uncoated (FUC) particles:*

Droplet depositions of 0.05 g of the Ag paste were applied into a boat and dried for 2 minutes. All samples were dried at room temperature and 70% RH.

* *Spherical/oleic acid coated (SOC) particles:*

Droplet depositions of 0.025 g of the Ag paste were applied into a boat and dried for 2 minutes. All samples were dried at room temperature and 70% RH.

5.3. Sintering process

The sintering process was developed using a two steps thermal profile (1) heating-dwell and (2) cooling, all without external pressure. The furnace was set at the sintering temperature, samples were then introduced and held for the pre-established dwell time, after which they were taken out the furnace and cooled down to room temperature. The process was configured so that the samples can be introduced directly into the set sintering temperature from which they will start heating until equilibrating its temperature with that of the furnace. Figure 16 shows the actual oven profile (solid line) and the sample's measured temperature profile (dashed line).

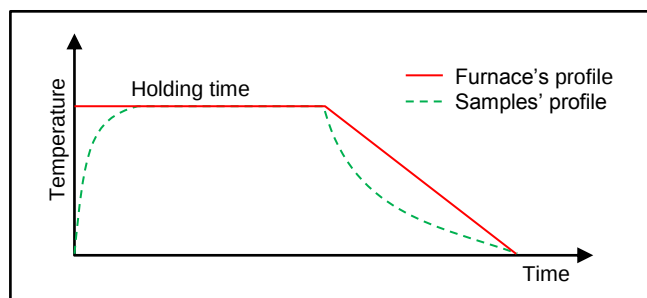


Figure 16. Schematic temperature profile for the sintering process.

The set parameters for the sintering tests were temperature, time and atmosphere as given in Table 5. The controlled argon (Ar) and the air atmospheres were evaluated to study its effect on the sintering mechanisms.

Table 5. Parameters for Sintering samples processing

Atmosphere	Open air atmosphere									
	Holding temperatures									
Holding time ► Paste type ▼	200°C		250°C		300°C		400°C		500°C	
	10 min	30 min	10 min	30 min	10 min	30 min	10 min	30 min	10 min	30 min
Spherical Unc.	-	-	-	-	✓	✓	✓	✓	✓	✓
Flaky Unc.	-	-	-	-	✓	✓	✓	✓	✓	✓
Spherical Coat.	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Atmosphere	Argon controlled atmosphere									
	Holding temperatures									
Holding time ► Paste type ▼	200°C		250°C		300°C		400°C		500°C	
	10 min	30 min	10 min	30 min	10 min	30 min	10 min	30 min	10 min	30 min
Spherical Uncoat.	-	-	-	-	✓	✓	✓	✓	✓	✓
Flaky Uncoated	-	-	-	-	✓	✓	✓	✓	✓	✓
Spherical Coated	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

The samples were sintered in a Lindberg/Blue M tube furnace, model TF55035A, with a 2"x1¼" glass tube chamber. The setup of the sintering experiments with Ar is presented in Figure 17 where the samples were introduced into the glass tube with a thermocouple connected for temperature sensing. Thermal profiles were verified with a BK precision 715 data logger.

The Ar gas was injected through a rubber stopper (left side of the tube) with a hose, and exhausted from a similar connection in the opposite side (right side of the tube) as shown in Figure 18. The gas inlet and outlet connections of Ar were unplugged and the stoppers were removed for the air trials.



Figure 17. Setup for atmosphere control with the glass tube and hose connection

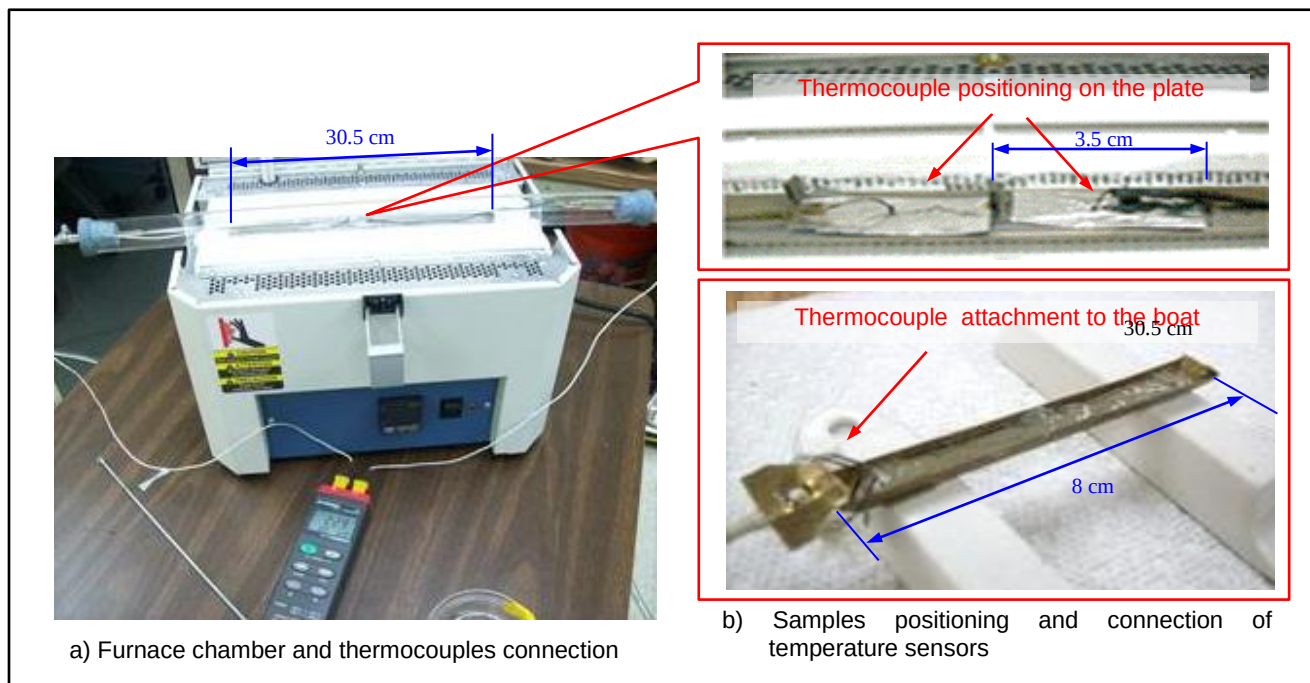


Figure 18. Thermocouple connections with holders and sample positioning inside the glass chamber

A semicircular cross section prismatic bar with $1''\varnothing \times 1'$ of dimensions of stainless steel was used as base for the samples inside the chamber. This piece of metal was included in the set-up to get a heat reservoir, i.e. to avoid the excessive temperature drop in the chamber with the sample insertion. Figure 19 illustrate the sample's positioning and the sensor connections in the tube chamber. For illustration purposes the schematic shows two carriers in the chamber, but they were processed one at a time in practice.

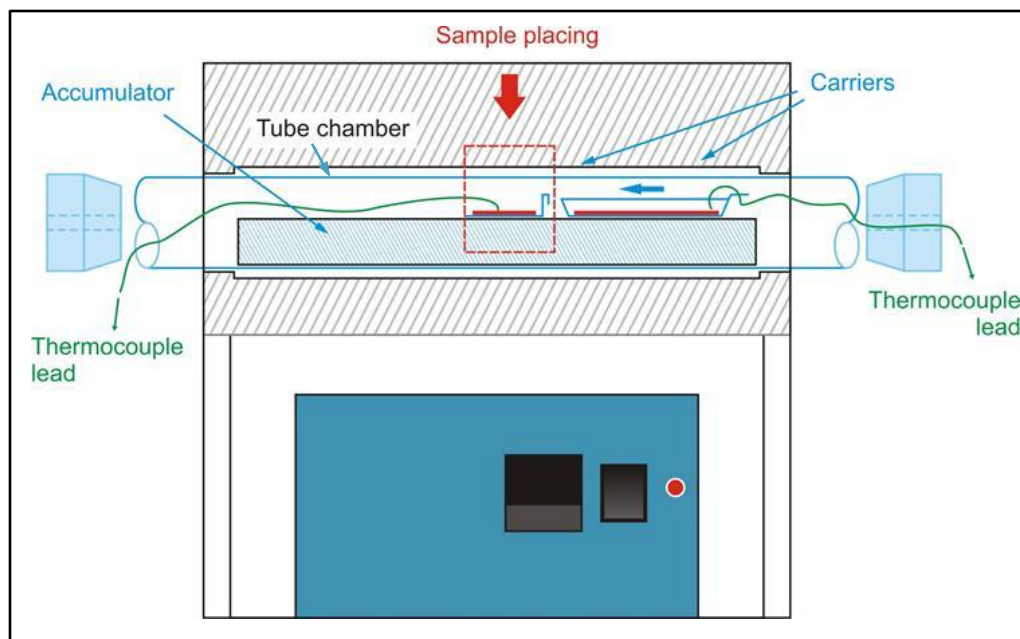


Figure 19. Schematic representation of the positioning and connection of samples in the tube furnace.

Samples were introduced into the tube furnace for the sintering trials following a programmed schedule considering a random distribution of the input variables: temperature, time, and atmosphere (see Appendix VIII and Appendix IX).

5.4. Characterization techniques

Three techniques were employed for characterization of the sintering process: differential scanning calorimetry (DSC), micrographical analysis by scanning electron microscopy (SEM), and microstructural analysis via X-ray diffraction (XRD). The following sections will describe each technique, findings will follow.

5.4.1. *Differential scanning calorimetry (DSC)*

Differential scanning calorimetry (DSC) is a powerful technique for thermal characterization of materials [61]. It was conceived to determine the specimens' melting and solidification response, such as onset temperature of phase transformation and the enthalpy of fusion.

The DSC equipment works with two cells (the sample and a reference) which are heated at a constant rate while maintaining the same temperature. One crucible contains the material of interest while the other remains empty (see Figure 20); these conditions suppose that there must be a net difference in the heat absorbed/emitted by this system, depending on the thermal stimulus (heating or cooling).

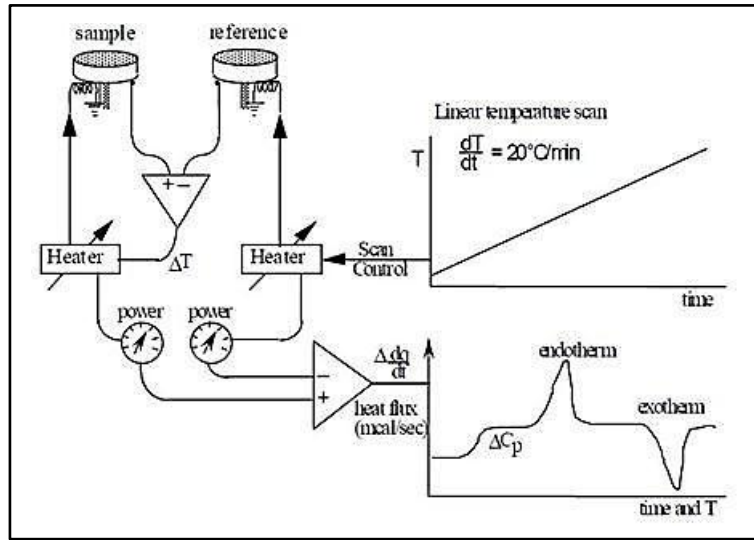


Figure 20. Schematic of operation principle the DSC [61]

The equipment registers the heat flow difference between the specimens [62] generating data that can be plotted, additionally it provides qualitative information. For instance, in the event that the sample experience a phase transformation it will be reflected as an endothermic or exothermic peak, if the data collected is plotted in a heat versus temperature or time graph.

As mentioned before, different material characteristics can be obtained as the material undergoes heating or cooling. For example, since the heat flow (dQ/dt) required to raise the temperature of the sample depends on the heat capacity C_p (Eq. 5.1), changes in this property can be measured by monitoring changes in the baseline (horizontal line) values.

$$\frac{dQ}{dt} = C_p \frac{dT}{dt} \quad (5.30)$$

In the case of a phase transformation, such as melting, an endothermic peak (in the plot) will be observed due to the difference in energy required to hold both sample and reference at the same temperature. When melting occurs, the beginning of the peak represents the melting temperature, where solid and liquid phases coexist as the melting process is progressing. The

curve slope towards the maximum of the peak, represents the amount of energy transferred to the sample. The peak maximum represents the end of the equilibrium melt region and the energy under the tail of the peak represents the energy needed to heat the liquid in the sample to the temperature of the furnace. Since the sample absorbs energy in order to melt, thus integrating the peak area will give the heat of fusion (ΔH_f) for this reaction. The maximum peak value and the peak height value will be mainly influenced by the sample weight [61]. Similar behavior is observed during solidification where exothermic peaks will be observed instead. Literature contains more information about DSC curves interpretation, which depends on the expected transformation, the set conditions of the profile, and the composition of the sample [63, 64].

5.4.2. Thermal characterization in the DSC

A TA Q20 DSC equipment available at the Nanomaterial's processing lab of UPRM was used to evaluate the thermal behavior of the as received silver nanoparticle powder.

Two basic approaches were employed for the thermal characterization of the sintering process through this technique. One group of tests was aimed at evaluating the progression of the sintering transformations with increasing temperature, and the irreversibility (or stability) of such transformations. Figure 21a presents two schematic profiles used for the tests which consisted in a triple cycle of heating and cooling, with ramps of 20°/min and 10°C/min respectively and with 600°C as the peak temperature.

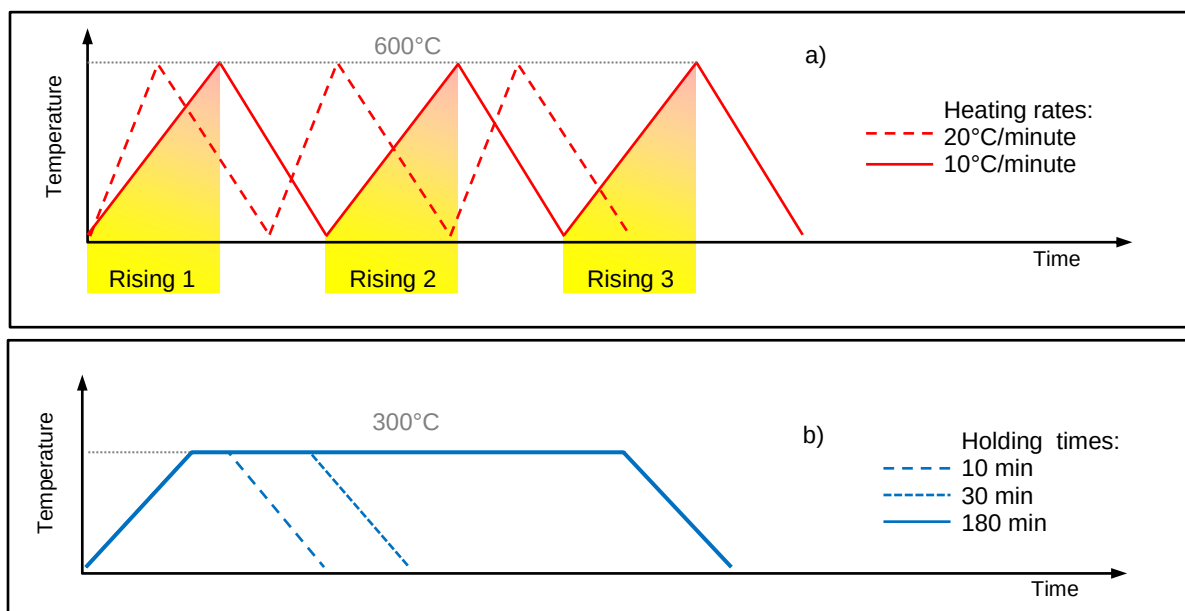


Figure 21. Schematic of the temperature profiles used for the DSC tests.

The ramp of 10°C/min were used because is the most common used in literature, while the ramp of 20°C/min is aimed to get closer to the expected real temperature ramp.

The other group of DSC studies was focused into assessing the progression of the sintering transformations along time, and to simulate the targeted conditions for sintering. Three thermal profiles were set and tested corresponding to three holding times. Similarly, Table 6 contains the parameters of the tests specifying their purpose, and the Figure 21b depicts the already mentioned thermal profiles.

Table 6. Parameters of the DSC tests²¹

Heating rate (°C/min)	T _{min} (°C)	T _{max} (°C)	T _{Holding} (min)	Cycles (#)	Objective
10	25	600	0	3	Thermal stability at high T (a)
20	25	600	0	3	Thermal stability at high T (a)
20	25	300	10	0	Simulate sintering test (b)
20	25	300	30	0	Simulate sintering test (b)
20	25	300	180	0	Sintering evolution with time (b)

²¹ All the DSC tests were run in a nitrogen atmosphere.

5.4.3. X-ray diffraction (XRD)

X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample.

This technique is based on the generation of X-rays (by a cathode ray tube), later filtered to produce monochromatic radiation, collimated (concentrated), and directed toward the sample. The wavelength (λ) of the final beam is similar in magnitude (~ 0.1 nm) to the planar spacing of atomic formations in crystalline solid specimens, several orders smaller than the wavelength of the visible light.

The incident beam must comply with geometrical conditions²² with the specimen (see Figure 22) to satisfy the Bragg's Law ($n\lambda = 2d \sin \theta$); which relates the wavelength of electromagnetic radiation to the diffraction angle and the spacing in a crystalline sample. These X-rays are diffracted, detected, processed and counted quantified for the subsequent analysis [65, 66]. Thus, all possible diffraction directions of the lattice should be attained by scanning the sample through a range of 2θ angles. The conversion of the detected diffraction peaks into d -spacings with standard data sets, allows the identification of the material because this is a distinctive property from each material [23].

²² This geometric conditions also constraint the incident angle to the range of $\sim 5^\circ$ to 70° .

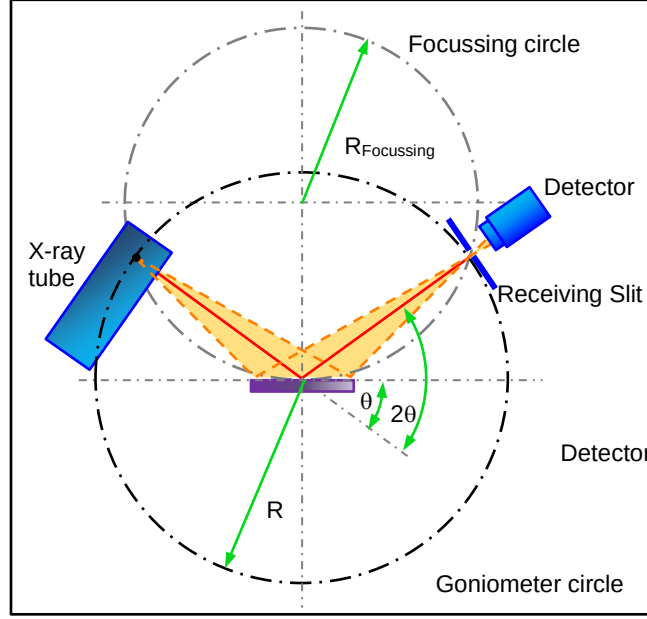


Figure 22. Basic geometry of an X-ray spectrometer [66]

The crystallite size (τ) can be calculated through the Scherrer's formula [66, 67], which relates the angular position (θ) of the intensity peak detected with the width at half maximum (β) of the same peak (if the spectrum is plotted).

$$\tau = \frac{K\lambda}{\beta \cos \theta} \quad (5.31)$$

where K is a shape factor (0.9). This expression is only valid for grains smaller than 100nm.

The spectrometers vary the incidence angle (θ) of the incoming X-ray beam to measure the scattered intensity $I_{(2\theta)}$, as a function of the scattering angle (2θ) of the diffracted rays, to later generate the diffraction spectrum [23]. The angular position (2θ) of the highest peaks in the spectrum is directly related to planar orientation of the atoms in the lattice of the sample (see Figure 22).

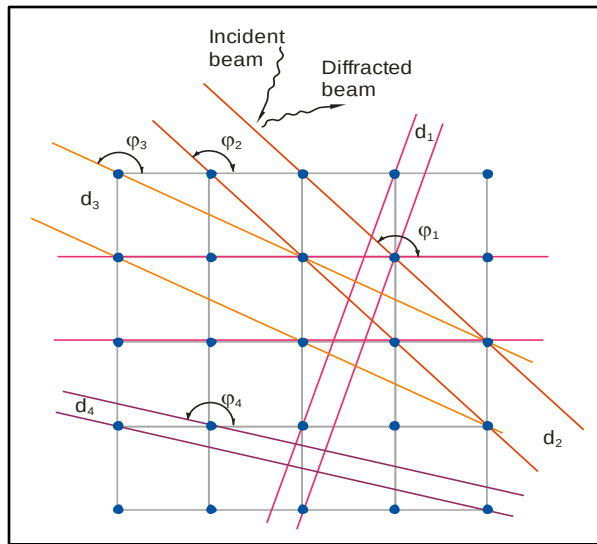


Figure 23. Planar orientation of the atoms in a lattice of crystalline material

The basic geometry of the most frequently used x-ray diffraction spectrometers is depicted in Figure 22. The rotations are performed by a goniometer, which comprises at least two coincident rotation axes, where the sample is typically mounted on the center, while the detector and/or x-ray source moves along the circumference of radius R (see Figure 22).

A X-ray diffractometer, SIEMES Beckman Coulter DU800 Spectrophotometer available at the Nanomaterials processing lab²³, with wave length $\lambda=1,54156$ and Cu $K\alpha$ radiation, was used for the crystallographic study. The collected information was used for material matching, to determine the presence of contaminants in the samples, and for crystallite size determination.

The parameters of the tests were adjusted, for all the samples, to 35KV with steps of 0.02° and 1 second dwell; the evaluated range was from 35° to 70° . Samples were taken as prepared from dried solutions and from the sintered specimens (see Table 7) to study their structural transformations.

²³ Department of Engineering Science and Materials of the UPRM

Table 7. Samples evaluated with XRD spectroscopy

Holding time ➤ Paste type ▼	Holding temperatures					
	300°C		400°C		500°C	
	10 min	30 min	10 min	30 min	10 min	30 min
SUC	✓	✓	✓	✓	✓	✓
FUC	✓	✓	✓	✓	✓	✓
SOC	✓	✓	✓	✓	✓	✓

A foil sputtering target of high purity silver was also X-ray tested for comparison and material matching, using the same parameters as with previous tests.

5.4.4. Scanning electron microscopy (SEM)

The SEM is a microscope technology which builds images using the interaction of electrons rather than light; SEM also uses electromagnets instead of lenses, which provide much more control in the degree of magnification giving as result a larger depth of field for the image. These forwarding technologies allow to the SEM a much higher resolution with the same higher magnifications. These facts have made it into a versatile and powerful tool for researching since its invention in 1950 [68].

A scanning electron microscope SE-SEM, Jeol JSM6100²⁴, equipped with a secondary electron detector (SE) was used in this study for characterization of powders and sintered samples as well as the raw powder for shape and topographic analysis of the nanostructures.

Conventional metallographic techniques imply sample preparation by grinding and polishing procedures; these procedures generate local heating, pressing, and material tearing which can enhance severe microstructure distortions in the samples' surface. Based on this,

²⁴ Research laboratory at the Mathematics Physics Department of University of Puerto Rico, Cayey.

samples were treated with no external pressure (no cross-sectioning nor polishing) in the preparation process for micrographic characterization, therefore it can be stated that our images are a faithful copy of the real topography of the samples.

Micrographs were systematically taken using the SE-SEM at 25KV, 8 mm working distance (WD) and 20 spot size (SS). Afterwards images were digitally processed and analyzed by using Adobe Photoshop CS5 Extended, V 12.0, a dedicated image edition software with a package image measurements; which was useful to perform the morphological analysis of particles and grains. The magnifications to take the pictures were carefully selected ranging from 100 to 60.000X in order to gather representative information of each zone in the sample, which later allowed obtaining an appropriate amount of information from each image. A total of 261 shots, named fields, were captured and they are briefly presented in Table 8. Field is a zone in the topography of a sample that can be captured; thus images different magnifications from the same coordinates in a sample are considered as the same field. Each analyzed field in this work comes from different coordinates and/or to different samples.

Table 8 . Summary of population of shots taken for image analysis

Magnification	Quantity	Condition	Quantity
100X	22	Raw particles	43
500X	25	Sintered at 250°C	13
1KX	26	Sintered at 300°C	129
5KX	30	Sintered at 400°C	35
10X	46	Sintered at 500°C	41
30X	41		
60X	28		
Others	43		

6. RESULTS AND DISCUSSION

This chapter presents the results from the sintering and characterization tests along with the concerning discussions. Properties of the raw Ag particles are presented, followed by the results of the sintering tests and characterization outcomes from the DSC and XRD experiments. A detailed evaluation of the SE-SEM micrographs is also presented with the evaluation of the structural transformations.

The Ag nanoparticles powder changed its physical appearance from a fluid paste to a “green compact” after drying (see Figure 24). This transformation happened by decanting of the paste without external pressure.

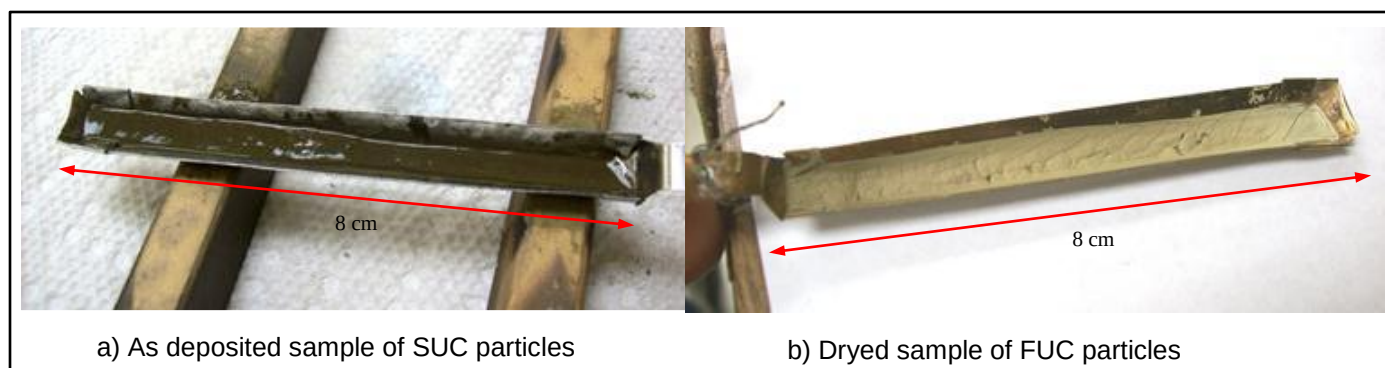


Figure 24. Ag paste change from a fluid like to a “green” powder compact after drying

Figure 25 shows two samples before and after sintering in their respective carriers. The dried samples look dark gray because of the presence of solvent remnants, while the sintered ones look (ivory) white. Their change from a powder compact (green compact) state to a continuum after sintering is evident from the shrinking which is the indicator of a consolidation process.



Figure 25. Physical appearance change (in color and size) of the samples through the sintering. Samples of SUC particles before (top) and after sintering (bottom) at 500°C (left) and at 300°C (right)

6.1. Differential scanning calorimetry (DSC)

The results from the DSC tests are presented considering two groups of analysis (see Figure 26): the first group evaluates the temperature dependency and stability of the structural transformations of the material, while the second presents the time dependency of the transformations as well as their results at the target conditions.

Figure 26 shows the results for the triple cycle profile examined at a ramp of 10°C/min. The equipment captured the data by sections, which resulted in the piece wise appearance of the curves. All data is represented in overlapped curves for a better analysis and comparison in Figure 27, where the successive curves for the triple cycle profiles are presented, for the 10°C/min ramp in (a) and the 20°C/min ramp in (b).

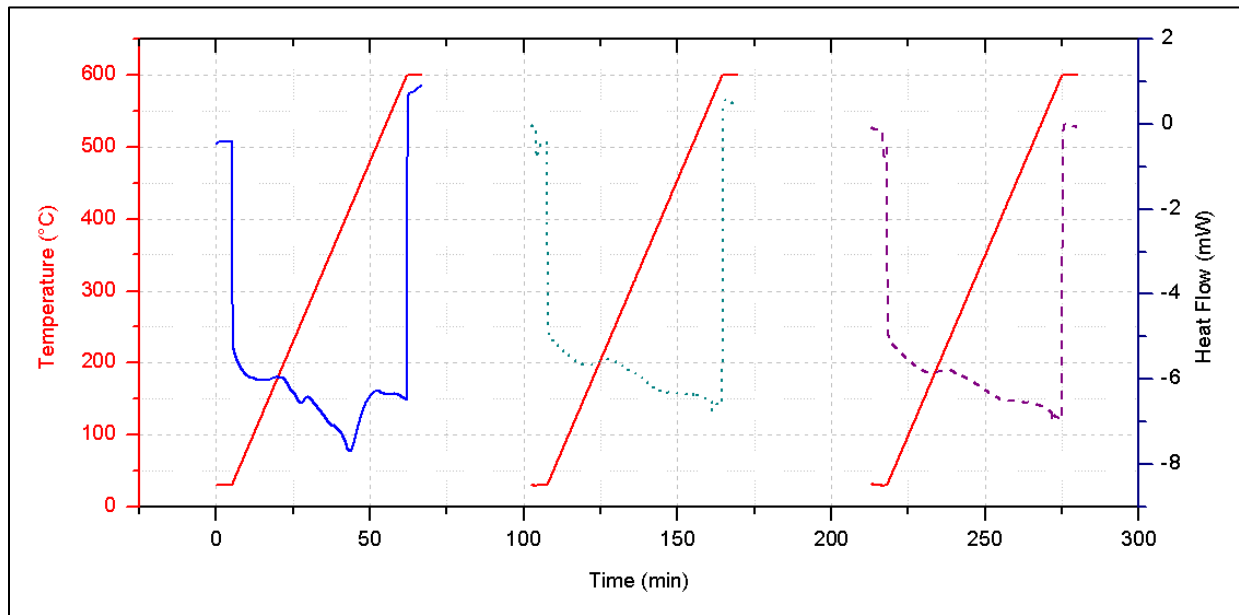


Figure 26. DSC traces of the with runs of thruple cycle test at 10°/min ramps

Both graphs in Figure 27 presents a red solid line which is the thermal profile followed during the test. Rising 1, 2 and 3 are the curves corresponding to the heat flow absorbed/ejected by the sample during the heating stages of process (see Figure 21).

It is believed that the low heating ramp (of 10°C/min) exerts an effect equivalent to the coarsening effect on the surface atoms at low temperatures, while the high heating ramp (20°C/min) produces an effect similar to a thermal wave that simultaneously excites the internal and external atoms of particles, generating massive diffusion and a massive energy emission. This is the reason for the big difference between the exothermal peaks in both plots. Additionally, the thermal inertia²⁵ of the system [69] with the 20°C/min ramp (Figure 27b) also influence in the aforementioned difference.

²⁵ Thermal inertia is how easy a material can change its surface temperature when exposed to a heat energy source. It depends on the temperature difference and on physical material properties such thermal conductivity (k), density (ρ), and heat capacity (c). *Thermal inertia* = $k\rho c$ (WJ/m⁴K²)

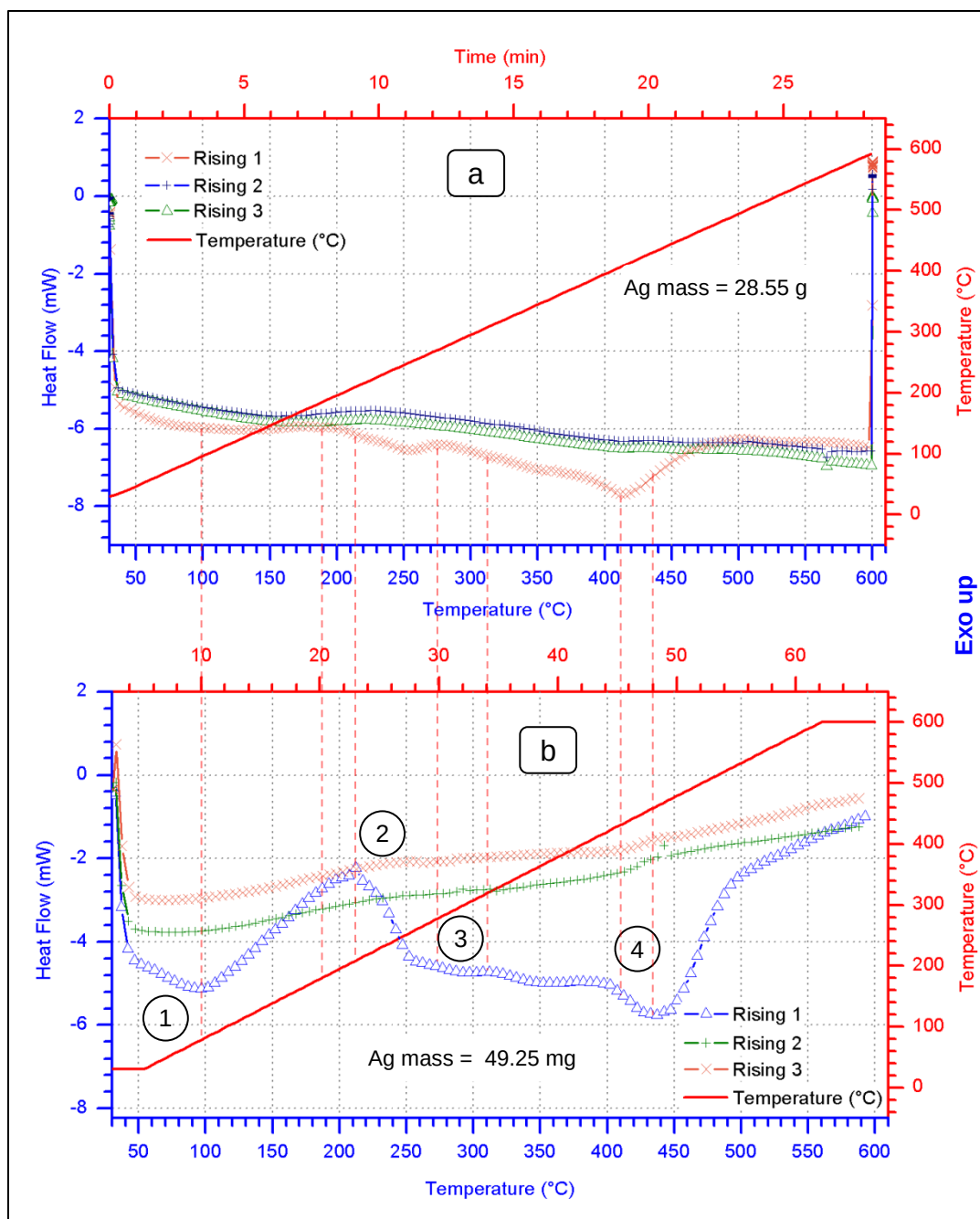


Figure 27. DSC traces of SOC particles resulted from the thermal tests run according to the scheme showed in Fig. 21a, for temperature dependence and stability evaluation

Four zones are distinguished in Figure 27b, which have four corresponding trace segments (one to one) in Figure 27a. The first zone (1) for each curve shows an endotherm, which corresponds with the moisture evaporation.

Rising 1 trace look quite different to rising 2 and 3 traces in both plots (see Figure 27) where significant peaks indicating transformations (zones 2,3, and 4) that only occur in the first temperature cycle. Rising 2 and 3 look very similar to each other confirming that effectively there are permanent transformations in the first rising. Graph (b) shows the zoomed peaks that can be matched with the smooth formations in curve (a).

Continouing with the analysis of Rising 1 trace, the second significant transformation occurs in zone (2) at $\sim 220^{\circ}\text{C}$, with a prominent exothermic peak (b), that can be barely matched in graph (a). The thirrd important transformation is revealed at $\sim 450^{\circ}\text{C}$ (zone 4) with an endothermic peak.

Oleic acid has a boiling point of 283°C [70] thus an endothermic peak should be observed, however it is not clearly detected in any of both plots; it should be around zone (3). In the other hand, the oleic acid, as capping agent is removed from the particles' surface which should be detected as an endothermal. This transition has been reported [71] to occur in two stages: a desorption of the extra oleic at $\sim 200^{\circ}\text{C}$ (endothermal phenomenon) and a dehydrogenation (or decomposition) of the remnants at $\sim 400^{\circ}\text{C}$ (endothermal phenomenon). The desorption is not detected as reported in zone(2), while the decomposition is effectively detected in zone (4). The decomposition of oleic acid produces graffitc residues which should have a negligible thermal effect in the sample in the rest of the test.

The three aforementioned endothermic processes are competing to be detected with the exothermic effect of the atomic re-arregement and re-crystallization produced by the sintering process. While atomic diffusion initiates the exothermic reaction, the oleic acid reactions are demanding for energy input to develope; then, consuming the energy it needs to evolve (the energy from sintering and the external energy).

The target conditions for the sintering process to formulate include a process temperature of 300°C; hence, the thermal analysis will be focused in the transitions which keep concordance with those conditions. Consequently, the effects observed over this temperature are just useful to show their irreversible condition which probe the sintering transformations already developed.

The heat expelled from the sintering exceeds the heat adsorption demands of the oleic acid desorption as it was detected in zone (2); that is the explanation for the exothermals in that zone, in both plots. It yields, the already mentioned peaks in zone (2) for both plots, sign the zones where a massive sintering process is taking place in the samples. However, the kinetics of the oleic acid reaction is not known yet; whereby the maximum exothermic point of the silver diffusion for sintering is still blurred. Even though, the process is still under the already set sintering temperature for the target conditions (300°C), which is positive to the purpose.

The results of the DSC tests on the sintering dependency on holding time (at the sintering temperature) are presented in Figure 28, where 10 minutes and 30 minutes holds are compared. The transitions observed during the ramping stage (see Figure 27) were also observed during these tests, where a peak temperature of 300°C was used. The exothermic peak was observed at ~230°C in both cases, and their difference in magnitude is attained to the fact that both samples contained different amounts of material in the crucibles. The similarity of the exothermic behavior confirms the sintering proces at the temperature range in which the diffusion process is being triggered.

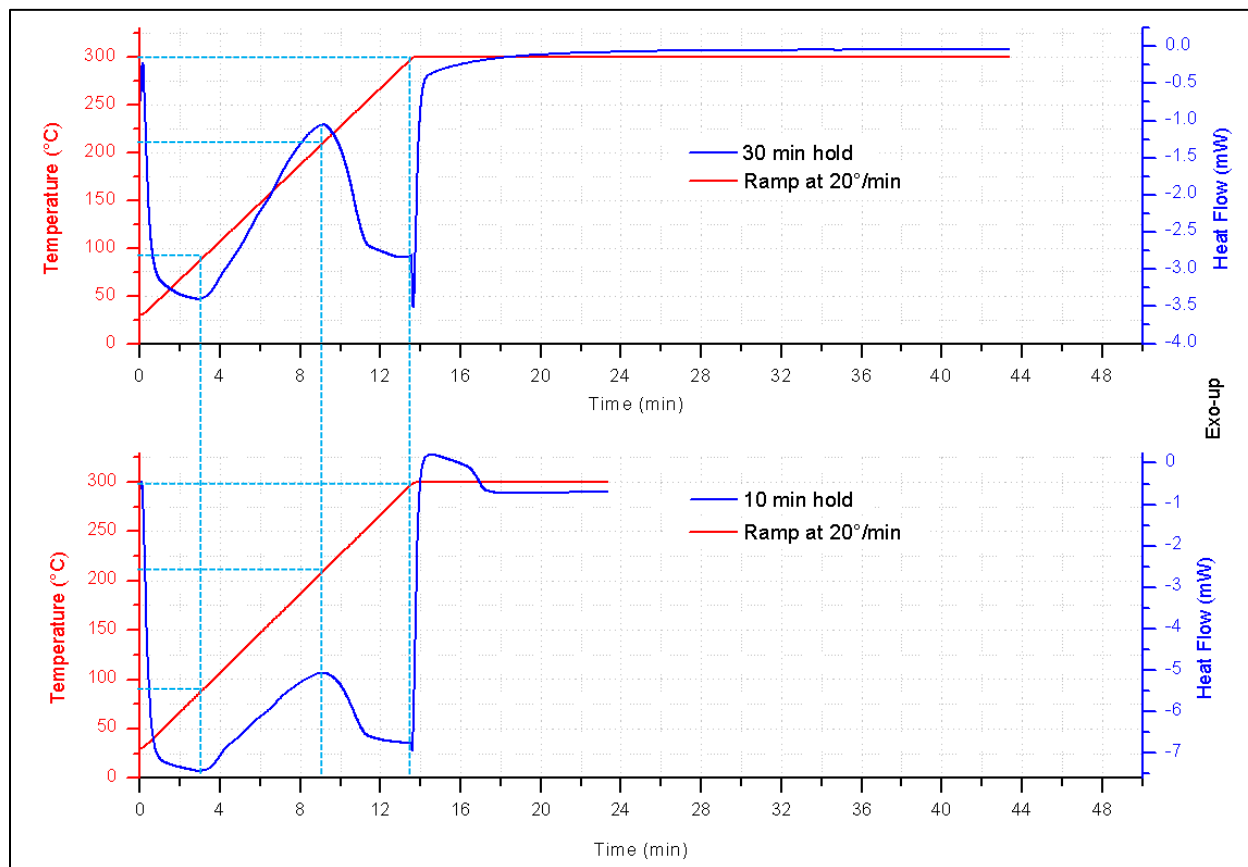


Figure 28. DSC traces of the tests performed to SOC particles as received, evaluating the time dependence and the target conditions

The test for temperature dependency of sintering showed that above 300°C, the organic compounds are still present and reacting. It is then expected that organic residues will be present owing to the fact that the test were performed at the same heating rate and not exceeding the 300°C limit which proved to be not high enough to completely eliminate the solvent. The temperature stability tests showed a similar behavior to the case of the particles evaluated in the temperature dependency test, i.e., one significant peak between 200°C and 230°C corresponding to the exothermic reaction associated with the atomic diffusion induced by the heat input.

6.2. X-ray diffraction (XRD)

XRD patterns corresponding to SOC particles and the sputtering target specimen were plotted together for comparison (see Figure 29 and 30).

Figure 30 shows the screen capture of the software Match!® where a peak comparison (from its internal data base of XRD patterns) with the examined pattern is presented .

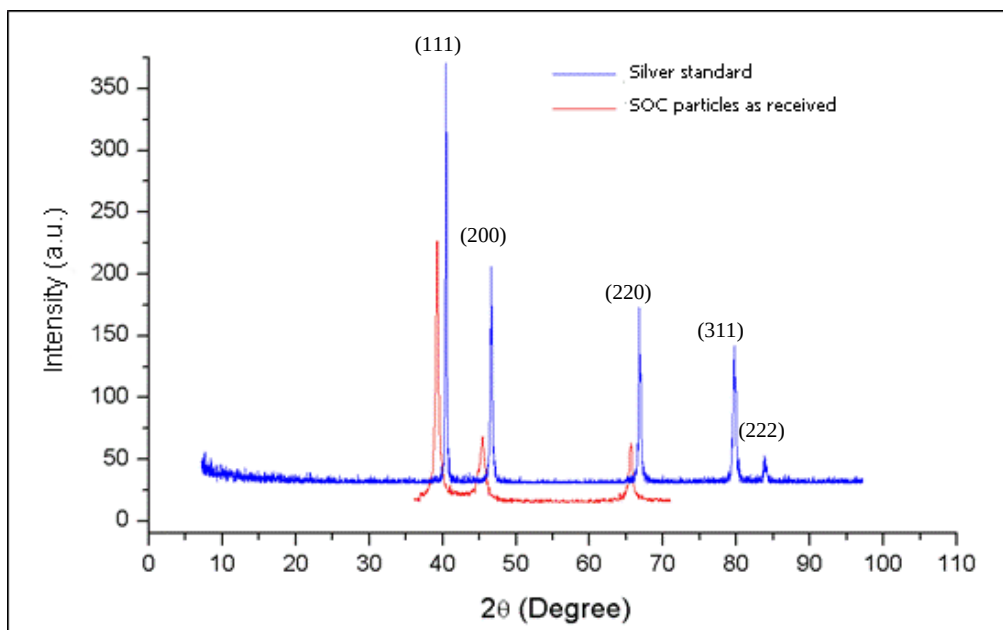


Figure 29. XRD patterns comparison between bare SOC particles and a silver standard (perspective arrangement)

The patterns from SUC sintered samples at different conditions are presented in Figure 31. The XRD results of 14 samples are presented and identified by codes specifying the sintering parameters: first, the temperature (300°, 400°, and 500°C), time (10 and 30 min) and a sample identifier (digit). These tests were useful to prove the non-existence of Ag oxide in all cases, from which it was also possible to postulate the absence of contamination in the raw material.

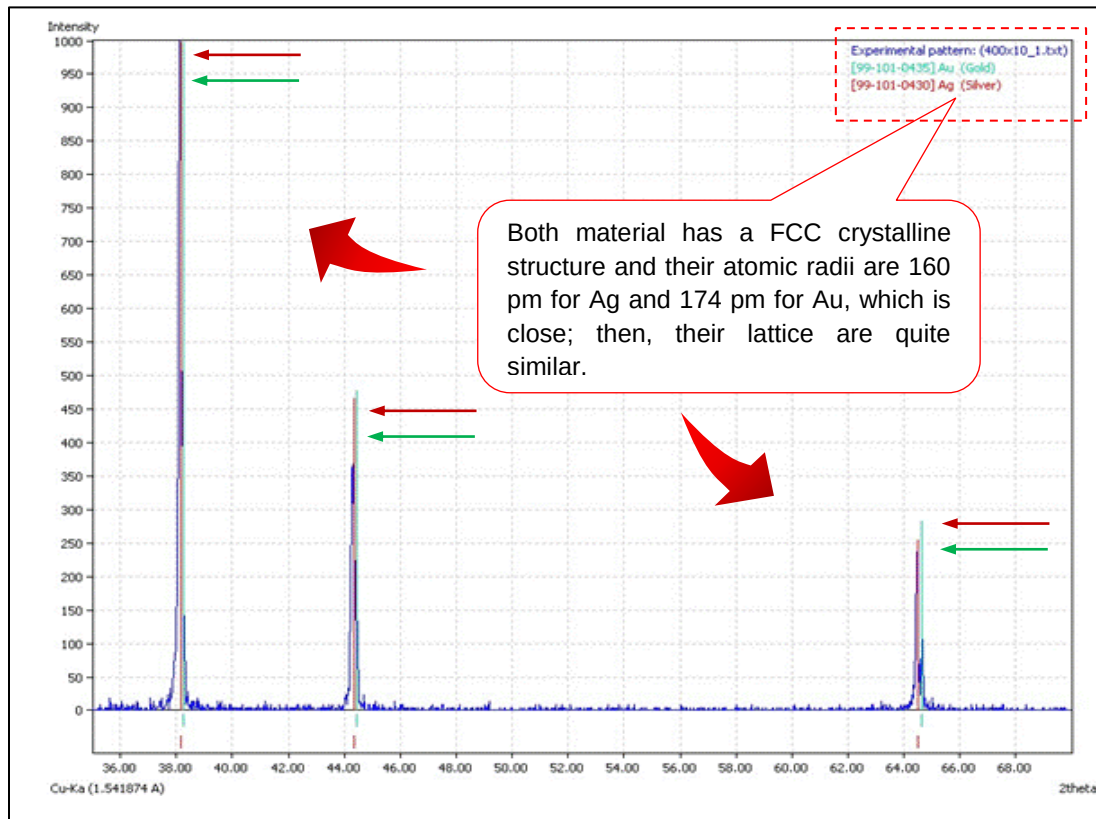


Figure 30. A screen capture of the Match!® software showing the pattern of a SUC particle sample sintered at 400°C for 10 minutes.

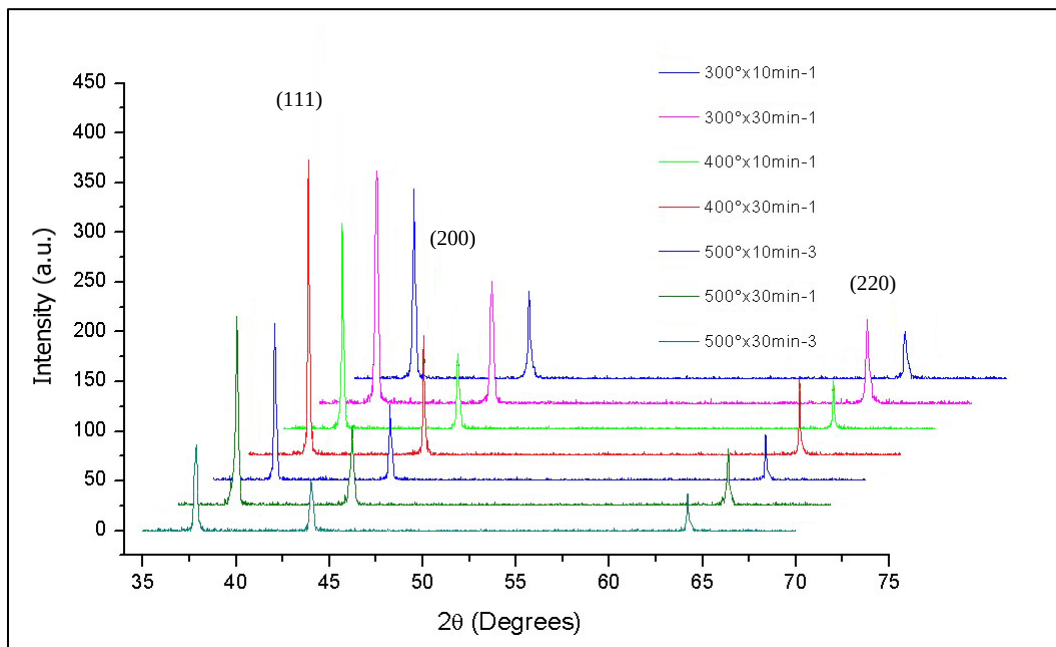


Figure 31. XRD patterns of samples sintered from SUC particles at different conditions in air atmosphere without oxide or contamination signs (perspective arrangement)

6.3. Scanning electron microscopy (SEM)

The aim of the SEM micrographs is to provide valuable information for the evaluation of the structural morphology of the particles and/or the material after sintering by the assessment of physical characteristics. This will be useful in determining the mechanisms of the structural transformations.

The results of different structural findings will be illustrated using representative images. Figure 32 gathers a key group of images from different magnifications and fields taken from the same sintered sample to better describe how the structures can be observed from different length scales. The distinctive structures from a sample fabricated by pressureless sintering of SUC²⁶ Ag particles will be then better associated with the physical transformations in the material.

A set of SEM micrographs from a SUC Ag nanoparticle paste sample pressureless sintered at 300°C for 30 minutes in air, is presented in Figure 32 (viewed at different magnifications). The images from this sample will be described and analyzed here on as a guide to understand the transformations and the mechanism of the sintering process. The image (a) is panoramic shot of the analyzed sample, showing the usual arrangement and the size tendency of the formed structures, their homogeneity and distribution. This same field was used to take additional captures at different magnifications to analyze the structural details and traits of representative zones in the material.

²⁶ SUC means spherical uncoated (see section 5.1 for specifications)

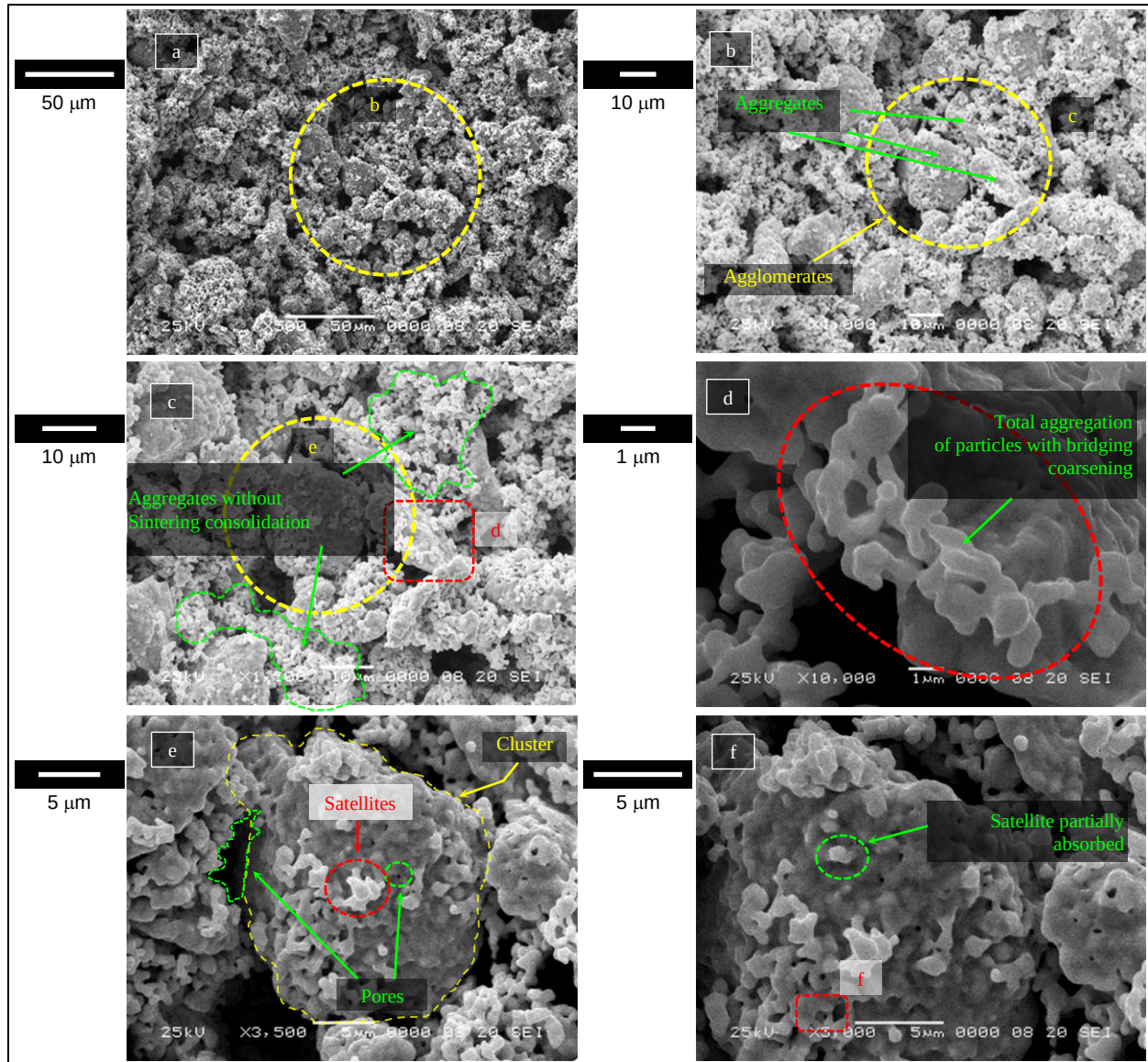


Figure 32. Graphical analysis of the structure of a SUC Ag-sintered sample processed at 300°C for 30 minutes in air. (a) Typical SEM micrograph of the resulting structure. (b), (c) Detail of characteristic formations which can range from agglomerates to weakly aggregated group of particles. (d) Main structural categories: cluster, satellites, and pores. (e) Partially absorbed satellite by the cluster. (f) Aggregation of satellites.

Image (b) shows details of the selected area (in frame (a)) where aggregates and agglomerates can be identified according to the characterization of their differences. Aggregates are the end result of an atomic diffusion mechanism which yields a dense formation at a higher

length scale; whereas agglomerates are defined by structures that result from weak interparticle joints, which can be reverted by physical means. It is known that the mechanical response of these compacts depends on the consolidation state of the structures (c and d), thus a methodology to quantify the state of the sintering mechanism by virtue of its progression of the aggregates into dense structures is critical.

Three main structural categories or classes have been identified and defined in our attempt to quantify the state of the sintering process for nanoparticles, namely clusters, satellites, and pores as illustrated in capture (e). A cluster is defined by the total consolidation of aggregates, which is given by the reduction of surface area of the incipient contacting particles. This trait can be measured by observing the reduction of convex surfaces on the particles [14]. A satellite is given by the partial aggregation of nanoparticles without the consolidation into a larger scale structure (see capture (d)). A pore is defined by dark areas which have no particles (see capture (e)).

An interpretation on how these basic structures constitute evidence of the sintering evolution may start from capture (c); there, the formation of clusters is apparent with the presence of satellites which may be in the process of being absorbed by the growing clusters or may be at a metastable state owing to the lack of physical compaction and/or lack of driving energy to continue with the sintering evolution. From this observation it is being hypothesized that the formation of clusters, therefore progression of sintering, depends on the close packing of nanoparticles prior to sintering, which may be inferred from the irregular formation of aggregates, appreciable in all captures (a) to (c). This initial accommodation maximizes interparticle contact enabling the possibility of a low temperature, pressureless consolidation process [15]. From a mechanistic stand point, the formation of satellites results from poor

packing of the nanopowder which results in the formation of necks but not providing the necessary physical contact to guarantee the activation of a massive diffusion mechanism thus impeding an effective densification into consolidated clusters.

Further inspection was performed at a higher magnification on a detail of capture (f) which was used to recognize structural transformation at the sub-micro length scale (see Figure 33). These observations were useful to compare these treats with respect to the transformations observed at the microscopic scale (see Figure 32 (d - f)).

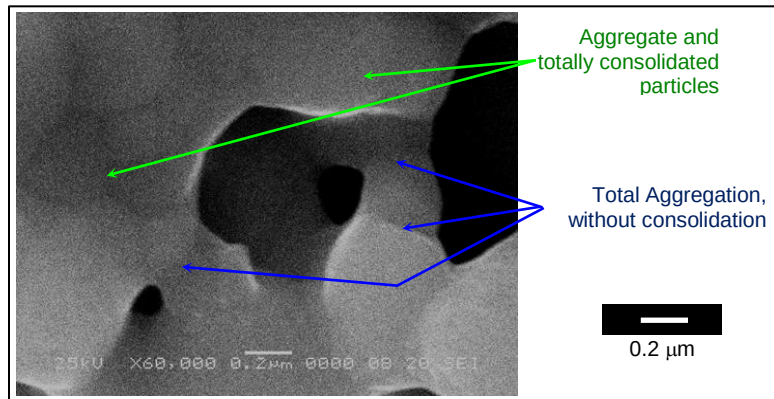


Figure 33. Structural details from Figure 32f. Total and partial state of consolidation of aggregated particles

Necks formed from different particles can be observed in Figure 33, where it is easy to appreciate how sintering continues to evolve until particles get blended, pushing the surface reduction and closing pores (consolidation).

After these insights from the sintering transformations, the analysis of the distinct traits is poised to serve as indicative of the prevalent densification mechanism. Therefore, the proper quantification of these traits (characteristics) and their classification into distinct categories provide the basis for a stereological analysis. As with any method, the most fruitful strategy for pattern recognition is to ask human brain how it classifies objects into categories. From this

basis, any developed tool will have to be able to classify objects or traits by digital image analysis using the same features as those used by the human brain.

Partially absorbed satellites, as shown in Figure 32f, and clusters with localized convex formations may indicate the lack of sufficient energy (either by means of surface free energy, sintering temperature or sintering time) to fulfill the required mass transport for sintering completion. All these discussed characteristics of the typical sintered samples, if properly quantified, could give insights of the sintering process.

Once the relationship between these structural features and sintering process parameters be established, the control of the die attach can be warranted.

For samples sintered from FUC and SOC particles²⁷ a similar image analysis was performed seeking relevant and prevalent formations, which may show the path followed by the particles in their stages through the process.

In this analysis, samples obtained by sintering of SOC Ag paste revealed a different structure, when compared with the findings given through the image analysis of the SUC samples. The micrographs analyzed from the SOC samples (see Figure 34) revealed no cluster formations when compared to the results found in the SUC samples (see Figure 32); where the structure showed a discrete like appearance. Additionally, Figure 34 shows a more homogenous topography, with more regular particle sizes (grains), where the so called satellites are not distinguished. Instead, a totally connected structure forming a dense material is appreciable.

²⁷ FUC means flaky uncoated, while SOC means spherical oleic coated (see section 5.1 for material specifications)

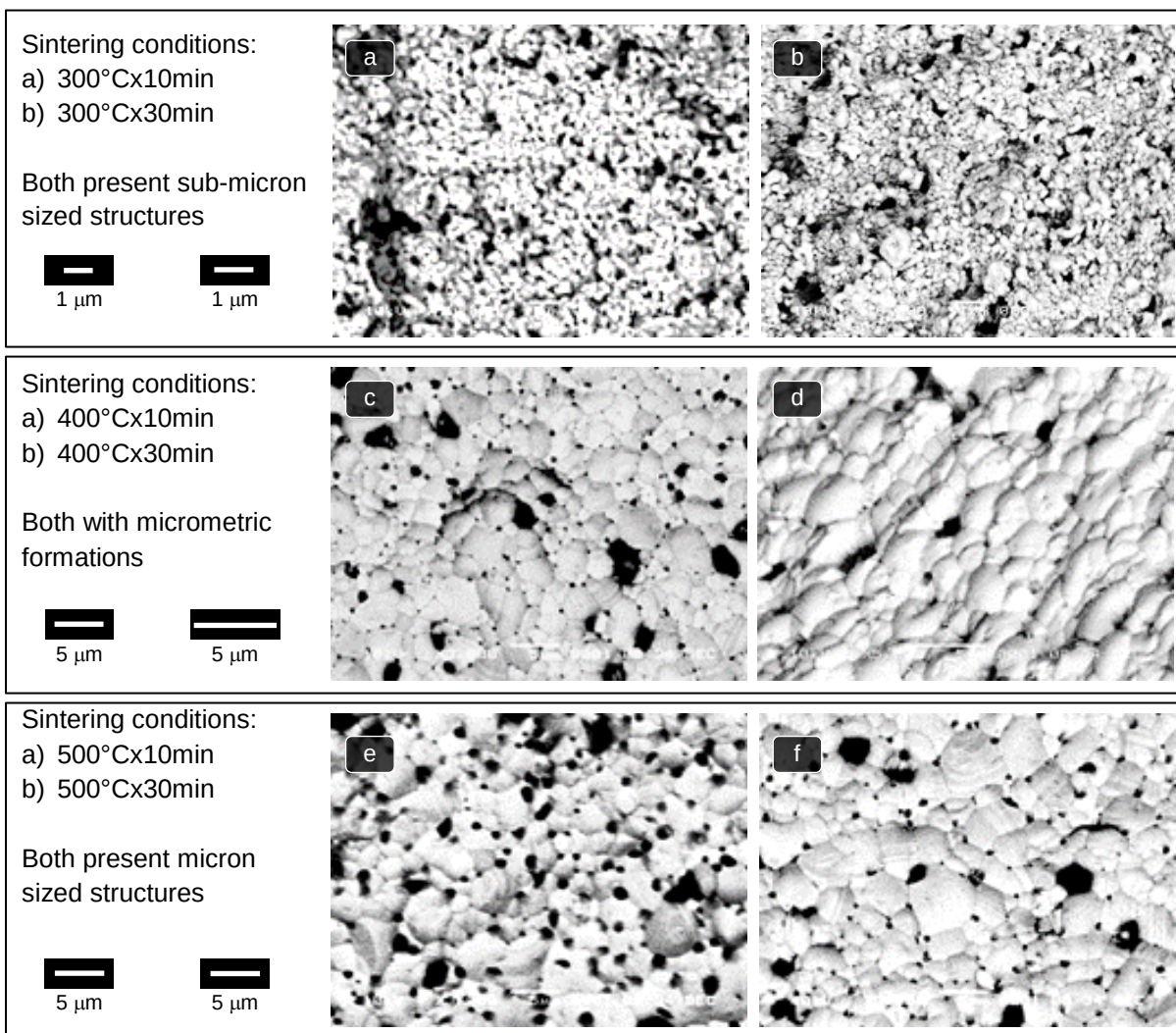


Figure 34. Samples fabricated from SOC Ag particles sintered in air at different conditions showing more homogenous and totally connected structure

FUC particles also showed connected structures but the porosity is more evident than those of SOC particles, with predominantly micron sized formations for all the testing conditions (see Figure 35).

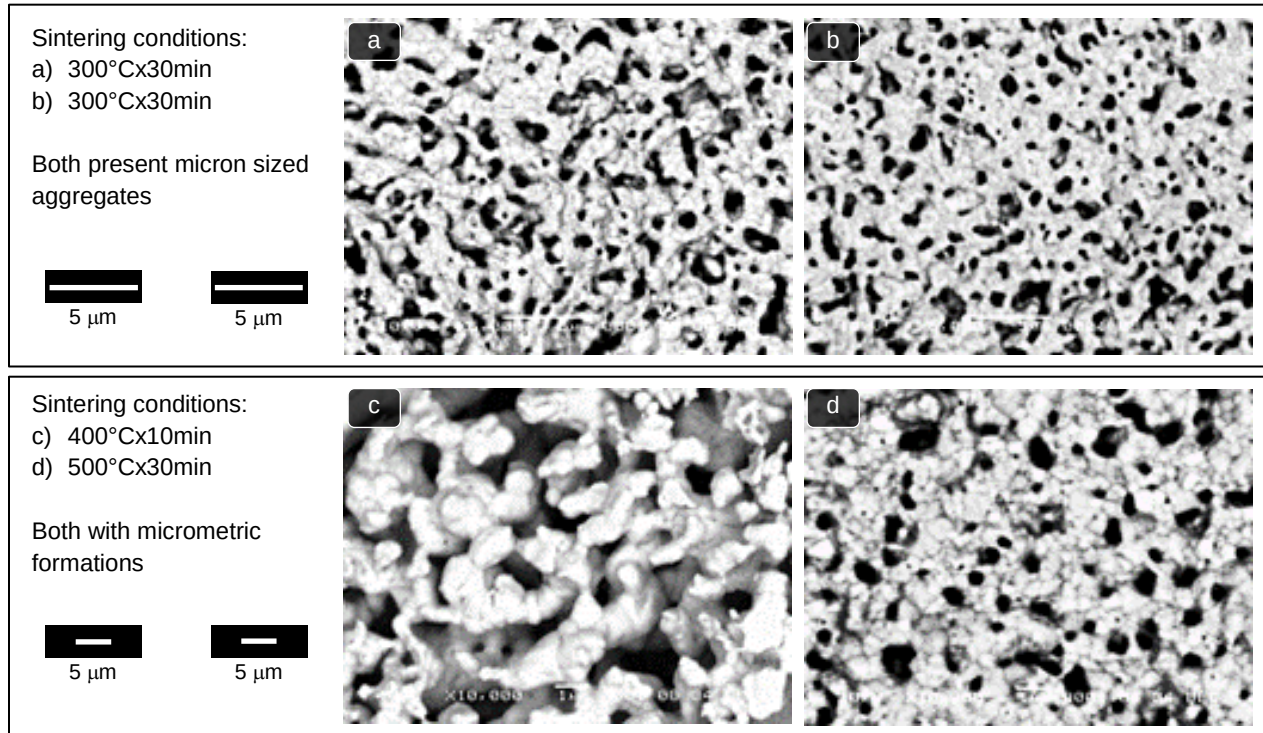


Figure 35. Samples fabricated from FUC Ag particles sintered in air at different conditions showing also a homogenous and connected structure

Following sessions are dedicated to extract more information from the imagery to assess sintering indicators.

6.4. Stereological technique

Feature assessment of images is an excellent tool to obtain information from materials, which can be accomplished by image processing. Image processing is a set of procedures that transform pixels characteristics and quantities so that they render a suitable representation for graphic or scientific purposes [72].

In the other hand, Stereology (supported on image processing) is the science that measures and extracts information from 2D images, to later application to 3D image formation [72]. That

is why principles and techniques of stereology and image processing were implemented as basis for the image analysis in the present project.

The actual evolution in sintering studies shows that the research on nanoparticle pastes or inks for electronic packaging has been mainly focused on low metallic loads owing to the fact that most common applications are for the consumer electronics sector and/or small signal electronics where currents are very low [19, 25, 55]. The characterization of these materials has been traditionally done by techniques such as TEM, XRD, and UV-spectroscopy, which are mainly focus at the nanoscale structures. The need of a reliable die attach material for high power and high temperature applications require sound joints at the micro-to-macro scale; therefore, a characterization of the structure at this length scale and its correlation with its mechanical, electrical, and thermal properties is much needed. Fundamentally, an efficient sintering process of metallic nanoparticles has to evolve from the nanoscale (particle level) to a denser structure at the micro or macro scale which can perform according to a set of required specifications.

Therefore, in order to study the effect of processing parameters on the behavior of a pressureless sintered joint, it is necessary to have a quantitative tool that can measure the structural evolution at the appropriate level. For example, in the resulting structure of a sintered powder it is possible to confuse between an agglomerated powder, with no particle integration (hence lack of mechanical integrity), with properly densified structures where sound interconnections may yield the necessary properties. For all these reasons, a tool capable of distinguishing these scenarios is important for the advancement of sintering as a reliable interconnection process for electronic packaging.

6.5. Qualitative analysis

The image analysis is guided into study the grain size as the feature that directly relates with the mechanical properties of the material. The previous observations (section 6.4) were useful to capture the structure at sub-micron and micron scale of the sintered samples; however, the application performance will be evaluated at the macro-scale. Certainly, there is a length scale which supposes to be the bridge for the gap between the discrete knowledge of nanoscale and the continuum and applicable macroscale. That is the mesoscale and it is not a specific length scale to define, but it is supposed to be the range in which the appropriate junction of the sub-micro and micron scale structures offers their best performance for the application. The mesoscale is a new challenge for the scientific community for next years [73] to fill the gap between the atomic and bulk state of matter; then mesoscale contains relevant information for the understanding of the pressureless sintering and its optimization.

Given the relevance of an adequate scale of analysis with the aim of getting valid results, a qualitative evaluation was done to compile characteristics of the sintered samples with critical influence in the final performance of the material respect to the application. Named evaluation will be a descriptive approach of the process' mechanisms. Table 9 contains a brief and global registry of this descriptive analysis which will be in detail explained.

The physical qualitative characterization of the sintered samples provided additional information about specimen's constitution. Macro-scale inspection of the samples, and their physical characteristics were analyzed over the different conditions: temperature (300°, 400°, and 500°C) and atmosphere (air and argon) for the particles types (SUC, FUC, and SOC), as shown in Table 5. Changes in time did not show noticeable characteristics that could be registered.

It is worth clarifying that sintering tests yielded in solid, and well consolidated materials when the processing conditions met. However, results were quite different when any of the critical processing parameters failed (namely temperature, time, preparation, and preservation), resulting in a powdery consistency of the compact.

SUC particle paste (dark gray), with their grayish-white sintered appearance, always showed a tendency to consolidate the powder in a massive body (see Figure 36), with an acceptable hardness and rigidity when qualitatively (by bend) tested. This condition is registered in Table 9 as Fractionated in the column Conforming II. The homogeneity of the observed structure (in micrographs) was registered as Conforming I.



Figure 36. The consolidation of all particles in a SUC paste (left) changed to a single body conformation (right) after sintering; clearly apretiable by the compact shrinkage attained.

Table 9. Qualitative assessment of properties of sintered samples, decisive to determine the best conditions to obtain superior results

SINTERING PARAMETERS			Color	MICRON-SCALE	MESO-SCALE		MACRO-SCALE	
Type	Temperature (°C)	Atmosphere		Structure	Packing I	Conforming I	Conforming II	Consistency
SUC	300	Air	Greyish white	Discrete	Porous	Non-homogeneous	Continuous	Hard
	400	Air	Ivory white	Discrete	Dense	Non-homogeneous	Continuous	Hard+
	500	Air	Shinny white	Connected	Dense	Non-homogeneous	Continuous	Hard++
SUC	300	Argon	Greyish white	Discrete	Porous	Non-homogeneous	Continuous	Hard
	400	Argon	Greyish white	Discrete	Dense	Non-homogeneous	Continuous	Hard
	500	Argon	Shinny white	Connected	Dense	Non-homogeneous	Continuous	Hard++
FUC	300	Air	Yellowish white	Connected	Dense	Homogeneous	Fractionated	Hard
	400	Air	Ivory white	Connected	Dense+	Homogeneous	Fractionated	Hard+
	500	Air	Ivory white	Connected	Dense+	Homogeneous	Fractionated	Hard++
FUC	300	Argon	Yellowish white	Connected	Dense	Homogeneous	Fractionated	Hard+
	400	Argon	Ivory white	Connected	Dense+	Homogeneous	Fractionated	Hard+
	500	Argon	Ivory white	Connected	Dense+	Homogeneous	Fractionated	Hard++
SOC	300	Air	Off white	Connected	Dense++	Homogeneous+	Fractionated	Hard++
	400	Air	Ivory white	Connected	Dense+++	Homogeneous+	Fractionated	Hard+++
	500	Air	Ivory white	Connected	Dense+++	Homogeneous+	Fractionated	Hard+++

Keys:

- * Type: type of silver nanoparticle evaluated.
- * Temperature and atmosphere: sintering conditions of the evaluated samples.
- * Color: helps to check the medium removal.
- * Micron-scale: disposition of the found structures if they were connected forming a net or they looked as isolated clusters.
- * Meso-scale: observations taken from micrographs with panoramic views (they are still in the range of microns). Conforming I is the regularity of the observed structures in the macrograph at that scale.
- * Macro-scale: observations made directly to the physical samples (their length scale is in millimeters). Conforming II refers to the tendency of the material to get integrated in a single body with sintering. Consistency is a descriptor which combines the resistance to scratching and bending.
- * The plus (+) represents a superior comparative measurement of the property.

Undesirable condition
 Desirable condition
 Irrelevant condition

Comparing the observations of the elements in Table 9 respect to the particles size (see Table 10), it is possible to appreciate that

there is a relationship between the particle size and the advantages in the final material gotten through the sintering process.

Table 10. Qualitative observations compared with the particle size

SINTERING PARAMETERS			SIZE	MICRON-SCALE	MESO-SCALE		MACRO-SCALE	
Type	Temperature (°C)	Atmospheres		Structure	Packing I	Conforming I	Conforming II	Consistency
SOC	300	Air	30 – 50 nm	Connected	Dense++	Homogeneous+	Fractionated	Hard++
	400	Air		Connected	Dense+++	Homogeneous+	Fractionated	Hard+++
	500	Air		Connected	Dense+++	Homogeneous+	Fractionated	Hard+++
SUC	300	Air / argon	~35 nm	Discrete	Porous	Non-homogeneous	Continuous	Hard
	400	Air / argon		Discrete	Dense	Non-homogeneous	Continuous	Hard+
	500	Air / argon		Connected	Dense	Non-homogeneous	Continuous	Hard++
FUC	300	Air	20-80 nm x 0.6-1.2 nm	Connected	Dense	Homogeneous	Fractionated	Hard
	400	Air		Connected	Dense+	Homogeneous	Fractionated	Hard+
	500	Air		Connected	Dense+	Homogeneous	Fractionated	Hard++
FUC	300	Argon	20-80 nm x 0.6-1.2 nm	Connected	Dense	Homogeneous	Fractionated	Hard+
	400	Argon		Connected	Dense+	Homogeneous	Fractionated	Hard+
	500	Argon		Connected	Dense+	Homogeneous	Fractionated	Hard++

SOC particles with their 30 to 50 nm in size, and with their oleic protective coating, can last more time without getting aggregated into bigger particles; this is an advantage that allowed them to get conformed into connected, denser, more homogenous, and harder sintered material, when compared to the other two type of particles (FUC and SUC ones, the uncoated particle types).

The reason why the uncoated particles did not get a better sintering evolution may be for the excessive early particle aggregation, which produces a particle size distribution widening. This widening is unavoidable, but when it is uncontrolled, it is believed to become into a drawback to the process efficiency. The wide particle size dispersion is expected as Maruyama [57] got in his tests; but Table 10 has shown that the more the size control is taken, the better are the results, as the gotten results with the SOC particles show in the qualitative analysis (see Table 9). In other words, the lower the particle size distribution, the better the results of sintering.

Ethanol and propanol (the dispersants in different tests) were found to be always reliable in easing the process do to its tendency to evaporate without difficulties at the tested temperatures. The uncoated particles were very sensitive and effective to initiating the sintering aggregation, resulting always in well-defined and manageable sintered bodies without leaving any residues in the carriers. This was a sign indicating that particles preferred their self-aggregation instead of sticking to the walls; that was the reason for the cohesiveness of the compact material resulting in a better conformation.

The FUC particles had a similar behavior to SUC, but with characteristic differences. They resulted in good hardness and consolidation, but their main characteristic was the impossibility to consolidate into a singular body as wanted (i.e. with poor conforming capability), thus producing isolated fragments of sintered material (see Figure 37). The solvents took part of this cracking effect, but it was not the basic reason of these fractures.

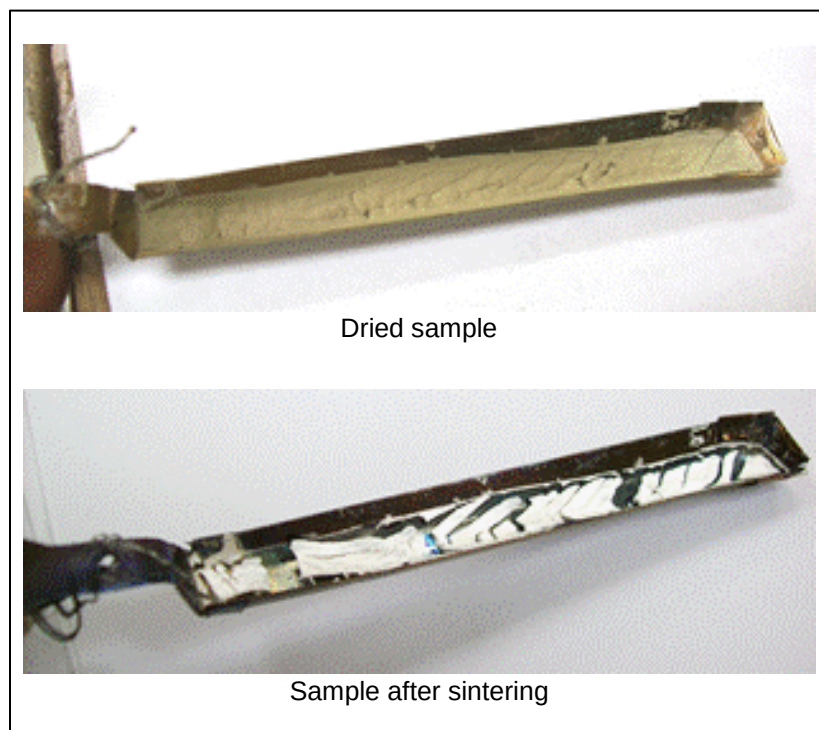


Figure 37. Fractioning of FUC samples occurs during drying and increases its effects through the sintering

The predominant and the main causes of cracking are complex interactions associated to the mixture characteristics which produce solvent migration during drying and/or during heating. This cracking effect is related to capillary effects, viscosity, surface tension, hydrostatic pressure, and hydrodynamic, just to mention but a few; this interactions induces separation of the mixture in phases while draining the solvent. Cracking worsens during heating due to the combination of particles' shrinkage and solvent evaporation, turning the drain zones into blow holes due to the escaping gases during the solvent gasification [74].

FUC particles are flake-like shaped with dimensions up to $1.2\mu\text{m}$, and when compared with the other type of particles, which are nano-sized, a noticeable difference is found. The forces that act during drying (and become bigger during sintering), try to agglomerate the particles into a single body (from a macro-scale perspective). Those forces are not enough to move the FUC particles as they do with the SUC due to their size. Their size and geometry are

the main causes that affect their mobility, hence, particles tend to get agglomerated only in their close proximity during drying stage, forming soft cracks that results in the fracturing of the sample during sintering. The formed blow holes constitute an additional barrier to the particles' agglomeration based on the fact that the sintering process evolve simultaneously in all particles when the general population of aggregates get formed with some size (in islands) and the blow holes surrounds them. The resulting attraction forces are not enough to bring these material islands together which is the main cause for the formation of the characteristic islands as depicted in Figure 37 for these types of particles.

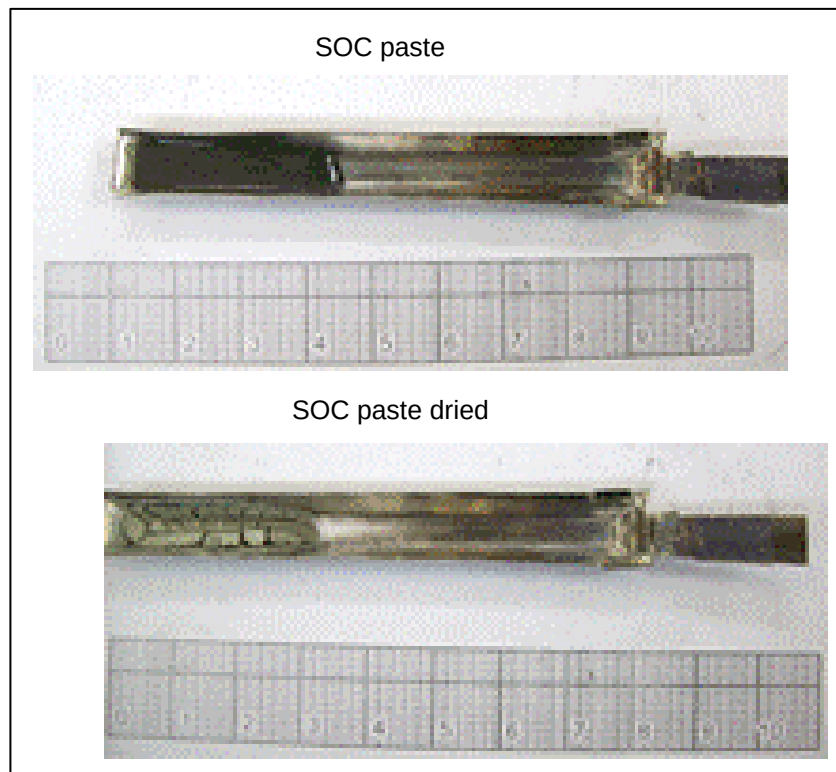


Figure 38. Fractioning in SOC pastes while drying

The fractioning effect in SOC sintered samples was also observed (see Figure 38) even though the particle size was smaller, i.e. their mobility during drying agglomeration should be better. This contrasts with the homogeneity of its microstructure²⁸ (see Figure 34), which should suppose a well conformed sample, i.e. a sample with a specific wanted form. The reason for the cracking in this situation is not the mobility of particles; in this case the solvent migration took a relevant part. The interactions between oleic acid (capping agent) and the isopropanol (solvent), eased the solvent segregation, generating draining channels forcing the crack appearance since drying stage in SOC pastes, as it occurred with FUC particles.

6.5.1. Summary of qualitative analysis

The consistency of the sintered material (especially in SOC particles) is one of the most important indicators of the sintering quality. The results obtained are very promising for the material performance. The adverse effects of cracking can be part of the optimization of the process to reduce their appearance. In fact, the findings from observation that SUC particles showed no cracking can serve as the basis for future development.

6.6. Image analysis

The existing image analysis tools can process images without significantly affecting the integrity of the picture; therefore the ability to capture features (measurable property) remains intact.

²⁸ This characteristic appears as homogeneous in Table 9 in the column Conforming II.

Gray level is the intensity value of a pixel and that is scaled from 0 to 1; these values have the potential of being used as measurable indicator in micrographs, permitting the categorization of structures. Hence these structures categories could be correlated with the control parameters in study; in this case, pressureless sintering. Consequently, this property will be used to perform quantitative image analysis.

The images of the structure and topography of the sintered samples were categorized and evaluated. A set of typical structures obtained by the sintering of the different types of silver nanoparticles at different conditions can be observed below (see Figure 39, Figure 40, Figure 41, and Figure 42). There the SUC (spherical uncoated) particles, the SOC (spherical oleic coated) particles, and the FUC (flaky uncoated) particles revealed their structures, and the differences are going to be analyzed.

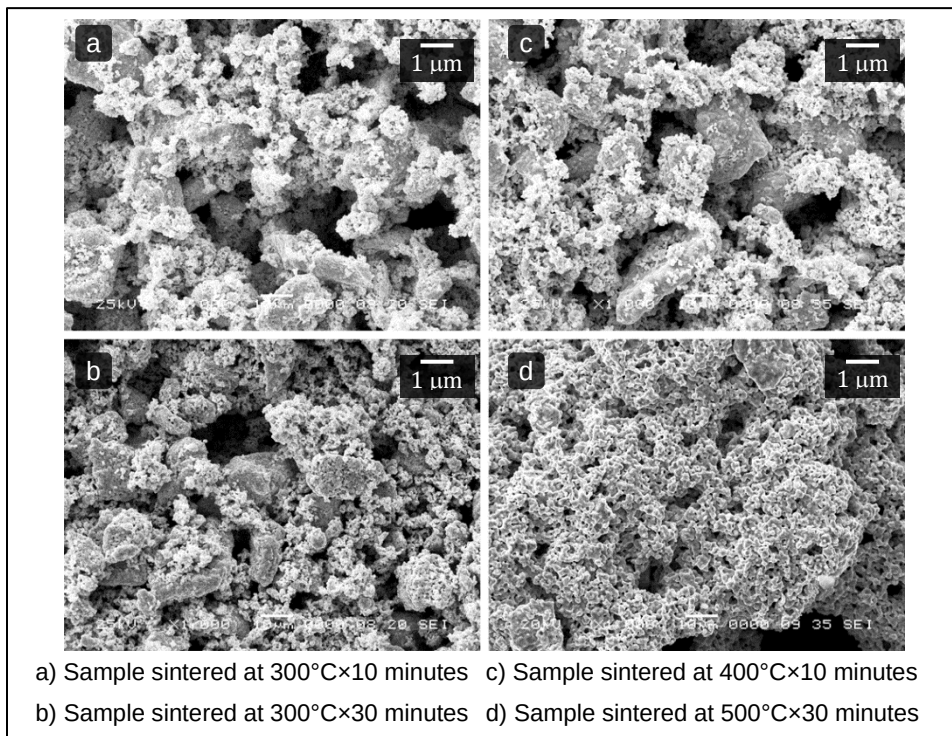


Figure 39. SE-SEM micrographs from SUC particles sintered in air.

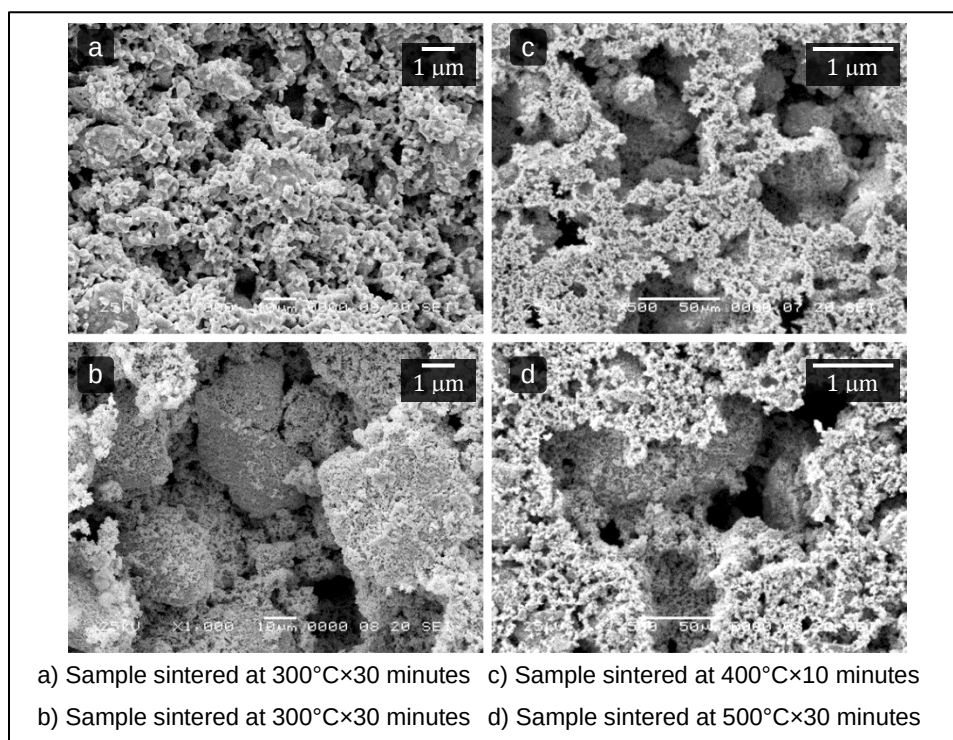


Figure 40. SE-SEM micrographs from SUC particles sintered in argon

Visual inspection of multiple SEM micrographs taken on SUC samples and processed across all experimental conditions revealed that it was possible to categorize the structures of interest (i.e. clusters, satellites, and pores) based on brightness (color) and size/shape (morphology). From inspection, it was very clear that, for example in SUC particles' structures, pores are given by dark (black) areas, clusters are associated with mid-tone grays, whereas satellites appear as the brightest structures (white). Analogue examination and deductions were taken from the FUC and SOC structures, but changing the features of interest.

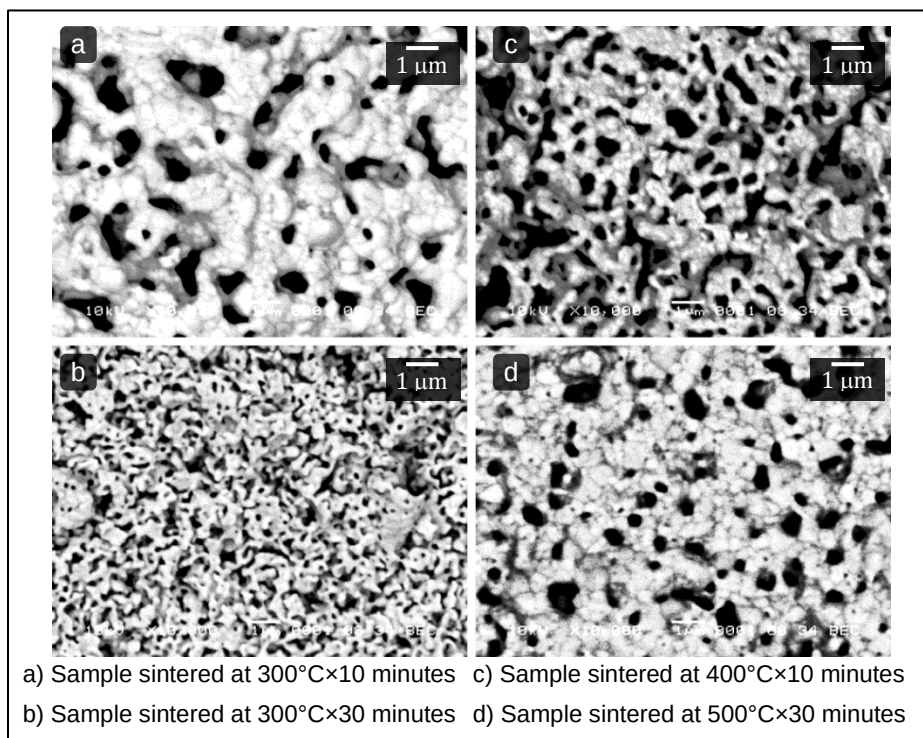


Figure 41. BEC-SEM micrographs from FUC particles sintered in air

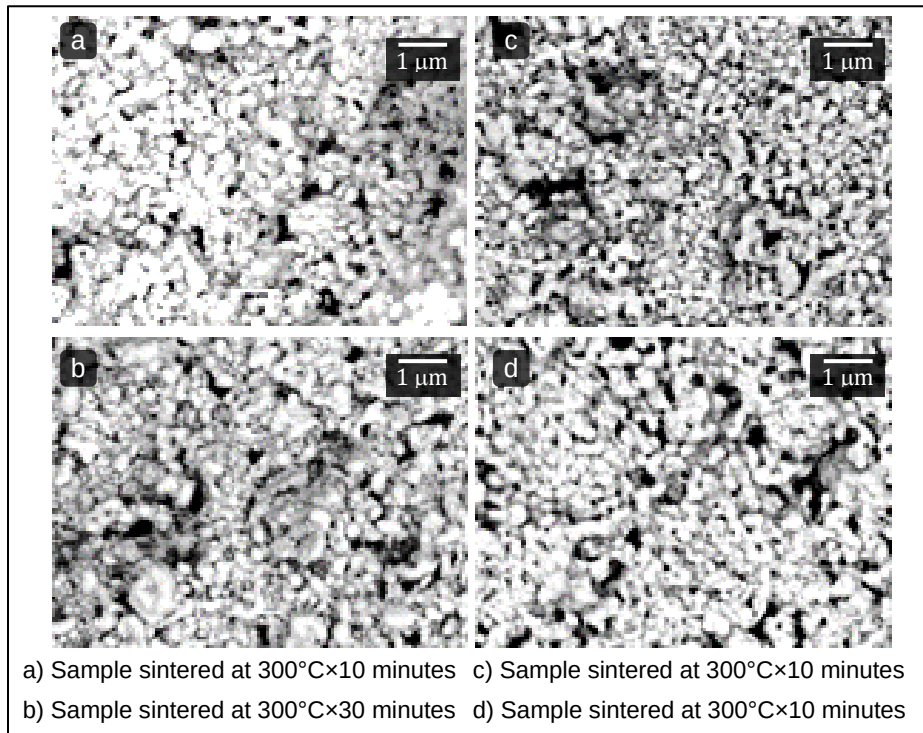


Figure 42. BEC-SEM micrographs from SOC particles sintered in air

From the aforementioned observations, an image examination procedure was developed and will be presented in the following section.

6.7. Image processing

The conversion of image traits into quantitative information to later generate conclusions on the pressureless sintering of Ag nanoparticle will be discussed in this section.

Three stages were developed for that purpose: a pre-processing stage aimed at the standardization of the image size and resolution, which included image normalization; a processing stage that deals with pixel management and classification, aimed at the contouring and measuring of the features; and finally a post-processing stage with the objective of data tabulation, debugging, and plotting.

The pre-processing was necessary to prepare the pictures to be analyzed. Image parameters were set as follows: image size 2000×1500 pixels, image resolution 200 pixels/cm, and the final size of each image remained in 10cm×7.5cm. Normalization is an enhancing procedure that consists of transforming the grayscale of the picture, so that the pixel intensity values occupy the entire grayscale spectrum which goes from 0 to 1. The technique sets the minimum intensity value in the image to 0 and the maximum to 1, while proportionally spreading the remaining values between the 0 and 1 limits. Figure 43 presents some results from the image normalization.

The processing takes care of eliminating irrelevant information while highlighting image features that facilitate the measurement acquisitions. A step called image-to-feature transformation was followed by a feature-to-decision transformation (which uses one or more features) to classify objects into specific categories.

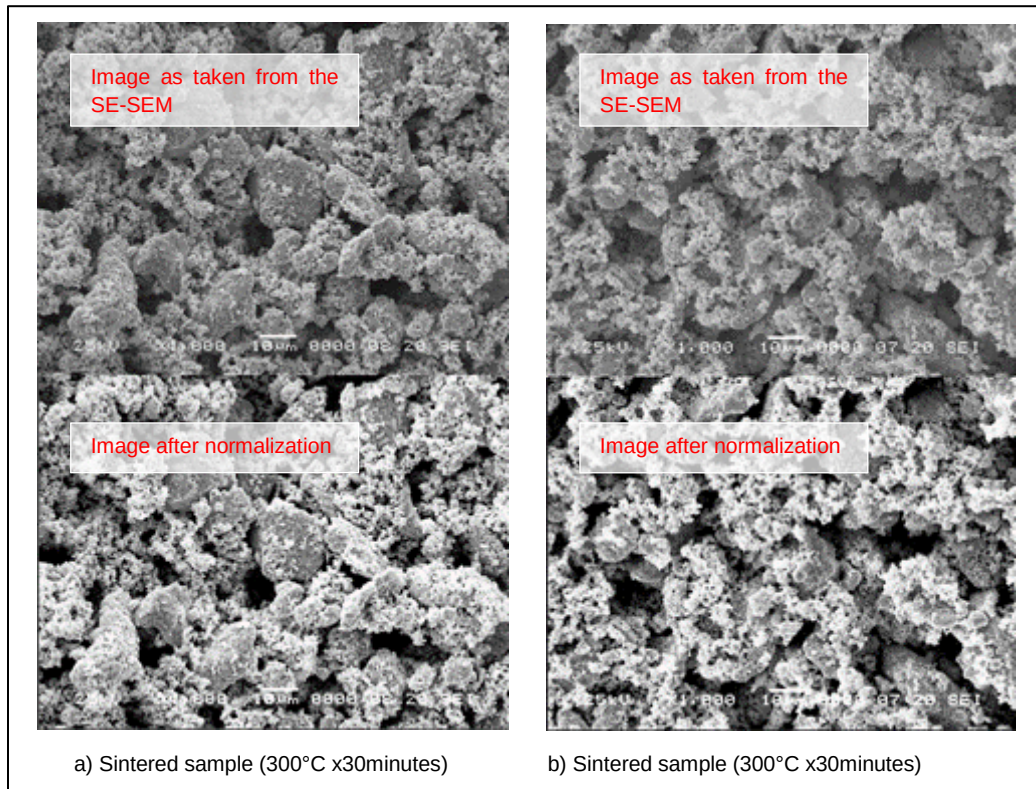


Figure 43. Image normalization of SUC samples sintered in air

The developed methodology was focused on defining features by the intensity level of the pixels and by using the already defined morphological criteria (see Figure 44) to distinguish and separate the objects of interest. A grey scaling transformation was performed to increase the contrast of the intensity levels, followed by a threshold transformation so that a binning operation could be performed. During this step, grayscale values within a defined range were all binned into discrete category as shown in Figure 44.

The surface reduction of a particle implies a tendency to evolve into a spherical shape as can be explained by thermodynamic arguments. The application of that concept to the image analysis can be evaluated as the perimetric reduction of the features (grains in this case) in their quest to attain the more energy favorable, spherical geometry.

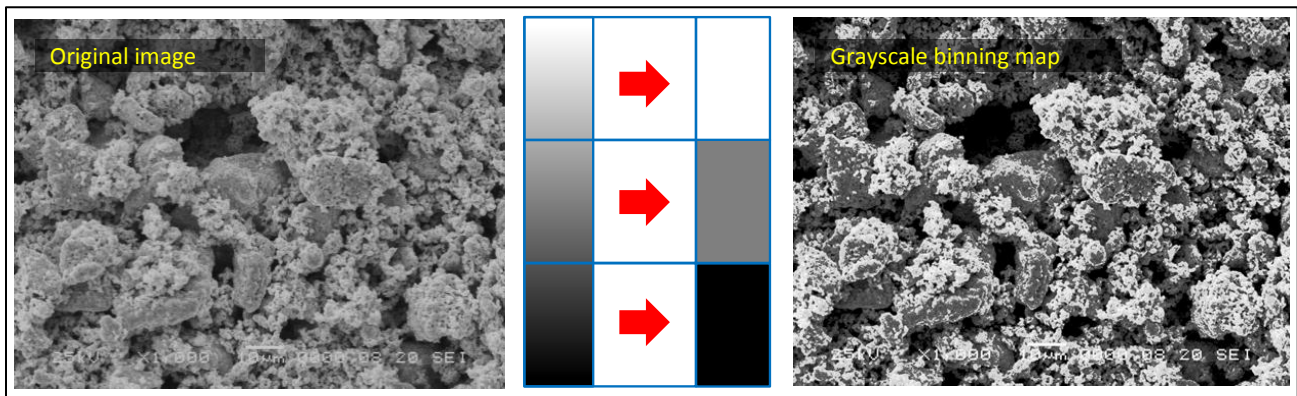


Figure 44. Gray level scaling transformation showing the binning of pixels based on a threshold.

The purpose of the morphological analysis in the present project is to assess the structural evolution of the sintering by measuring the effective diameter of the particles, as is defined in terms of the equivalent diameter of a circle (see Figure 45).

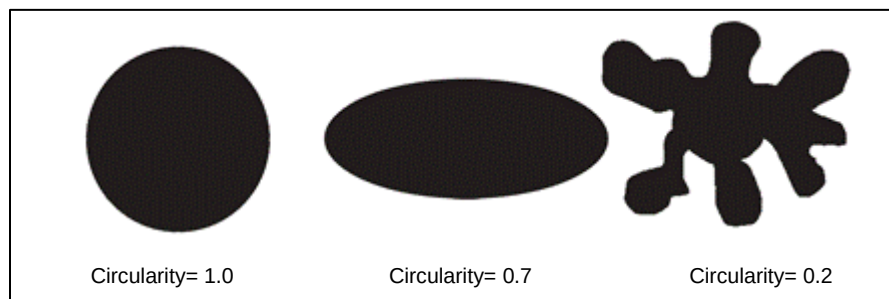


Figure 45. Three figures with the same area, different perimeter, and thus different circularity

Circularity quantifies the deviation²⁹ of a geometrical shape from being a perfect circle; it correlates the area (A) with respect the perimeter (P) as showed in Eq. (6.1), giving an index which goes from 0 to 1, 1 the circular shape [72, 75]. This parameter was also measured to the grain shape in the images.

$$Circularity = \frac{4\pi \cdot A}{P^2} \quad (6.1)$$

Finally, the perimeter of the particles was evaluated as a control parameter, since it is already implicit in the circularity concept.

Images were carefully selected to obtain the optimal magnification for the measurements where the appropriate level of detail was achieved. The digital analysis was carried out by separating, in different layers, the original images from the elements produced by the image processing, such as grid lines, contours lines, and shaped figures. These layers are invisible planes which are superimposed to the original layer to show references or highlight specific features. Rectangular grid lines were drawn over the images (in separated layer) to be used as reference to select and measure the elements identified as traits. Two types of squared grids were used: 1cm ×1cm and 0.5cm ×0.5cm (see Figure 46), depending on the sizes and sharpness of the features to be measured in the images. The elements selected to be measured were the grains laying on the intersections of the grid lines.

²⁹ Circularity is a dimensionless morphological parameter.

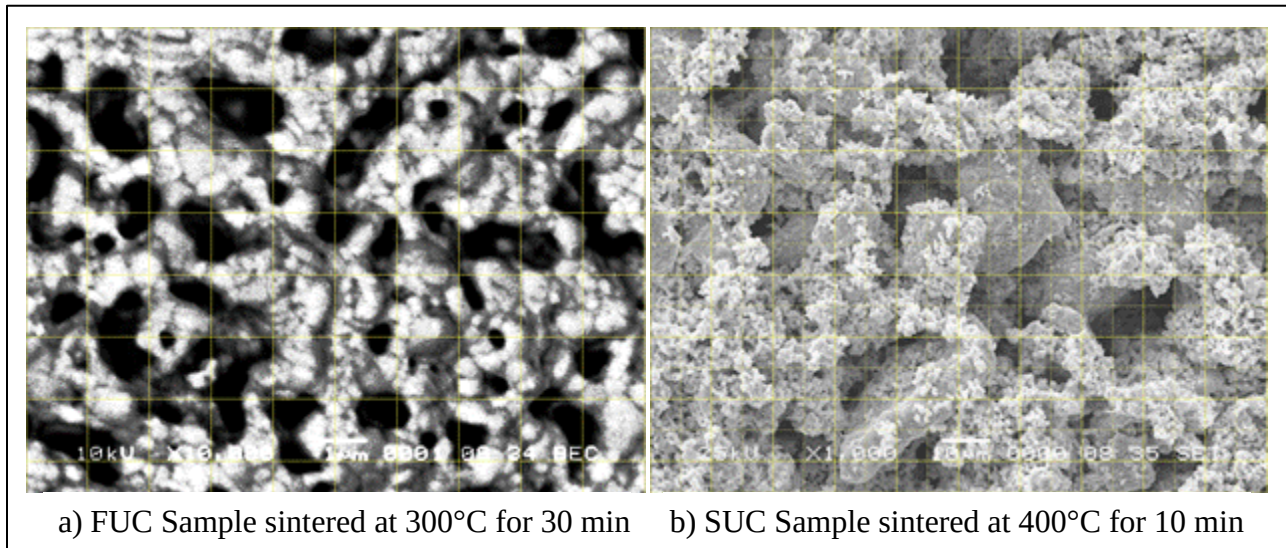


Figure 46. Grid lines used as positional reference to obtain the measurements of morphological features

Image processing was performed using the software Adobe Photoshop CS5 Extended®, and the output results were obtained through its platform Analysis. The contour of the grains, or features, was traced by manual silhouetting in individual layers (see Figure 47) to avoid the contour interferences and to reduce the misinterpretation. Different colors were used in the contours for distinguishing each element from others. Then, the image's scale, originally provided by the SEM and printed with the image, was used to generate the measurement scale (unit/pixel) for each picture. Measurements of interest were then captured: area, perimeter and circularity (all of them were automatically provided by the Analysis tool of the software). Consequently, three readings for each traced feature were registered, tabulated, and later plotted. The distribution of the population size was organized considering the control parameters: temperature, material type, time and atmosphere, and they will be discussed in next sections.

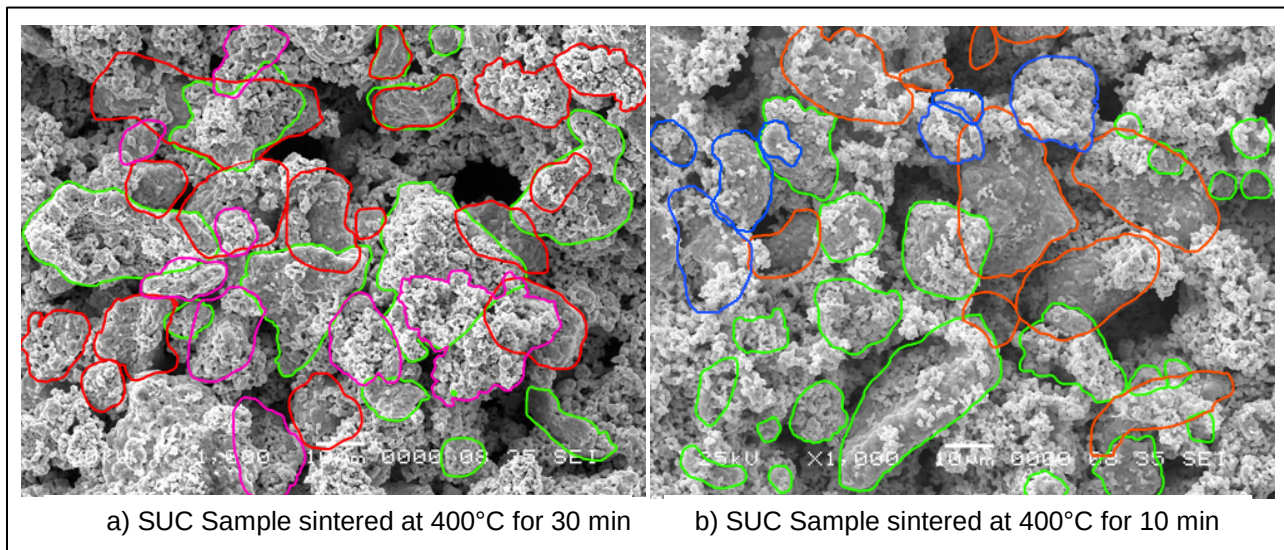


Figure 47. Features' contouring with the draw tooling of Photoshop CS5®

6.7.1. Post processing of image measurement data

Area, circularity, and perimeter measurements of the features in micrographs were organized and classified according to the processing parameters of the tests and the selected fields (see section 5.4.4). From these data sets the effective diameter was calculated and tabulated.

An important fact is that even though gathered information was plenty, in terms of particle and pore diameter sizes at different conditions, it was not enough to provide statistically supported numeric indicators. Different circumstances affected the statistical validity of the data. However, data is still valid as a reference for future works on the analysis of variables correlation or significance. Factors such as correct magnification to capture an acceptable amount of features, picture resolution, and the proper sample integrity reduced the quantity of samples and the available fields for analysis.

All micrographs were taken from as-fabricated samples without any additional preparation, to ensure the structure's integrity without causing transformations that could have been artifacts

of the handling/processing. Classical metallography could have produced such artifacts in the samples due to the heating and pressure exerted.

Box plots were chosen to analyze data trending for each kind of particle. “All against all”³⁰ data behavior was evaluated applying filters of “one way factor”³¹ for the plots; i.e., the plots were built using all available data, but considering only one factor (variable) at a time while the others were considered constant. The plots include: size distribution and circularity, temperature, time, and atmosphere. This type of analysis does not consider the interaction of factors in the results.

The first group of plots contains data on cluster size distribution in SUC samples; the next group presents data of pore size from FUC samples and finally, charts of pore size of SOC samples are also showed and discussed.

The size distribution of the raw particles was expected to be wide according to Maruyama’s findings [57]. The results shown in the qualitative analysis (in section 6.5) were coherent to that size presumption; thereby, the size distribution versus the average particle size prior to sintering are critical in the results of sintering progress and the sample compaction. Nonetheless, knowing the exact particle size distribution in the paste prior to sintering is a strong challenge, quite difficult to assess with the available equipments; because the high concentration of particles would need further dispersion or separation which is contradictory since the particles aggregation effect is in virtue of the high metal concentration in the paste.

³⁰ All against all applies when all data conditions are indistinctly analyzed together.

³¹ One way refers to that kind of analysis in which only one factor or variable is evaluated in an experiment neglecting the effect of the rest of variables, i.e. as if all the experiment were run with only one variable.

6.7.2. SUC samples: image analysis results

The distinctive responses of the SUC (spherical uncoated) particles are presented below. Figure 48a shows a box chart with the general trend of cluster formation, where average measurements are around 10 μ m of effective diameter; this is quite large when considering that the precursor particles were smaller than 100 nanometers in their nominal diameter. In fact, the mean cluster size is about two orders of magnitude bigger than the original particles.

Figure 48b depicts a box chart with the results of the measurements and calculation for the circularity of the clusters in sintered samples of SUC particles. The charts show the box have a bottom limiting percentiles indicating the value defining the 25% of the population; while the top limit is referencing the value at which the 75% of the measurements are placed.

The 1% and 99% percentiles ($\times$)³² show a representative limit for deviated data from the main concentration of the data population (the box); the mean point ($\square$), is placed at the mean value of the measurements, very close to the line reference where the 50% of data concentrate their values. As shown in the plot, the majority of the data lies inside the box whereas the majority of the dispersion is given by the remaining points. The normality curve associated with the data distribution allows appreciating the distribution of all points.

The mean of the circularity data is ~0.7 which is indicative of a quasi-circular shape, and consequently, a considerable uniform formation of the aggregates which form the sintered sample from SUC particles. Irregular shapes, as given by circularity less than 0.5, are indicative of a sintering mechanism which could lead to coarsening or densification without consolidation

³² The symbol enclosed among the parenthesis is used in the chart to sign a statistical parameter: ($\times$) for 1 and 99% percentiles, while ($\square$) marks the mean of the data and (-) the outliers.

(see Figure 45) since it is known the circular shape of the aggregates indicates an advanced surface reduction and consequently a more stable body.

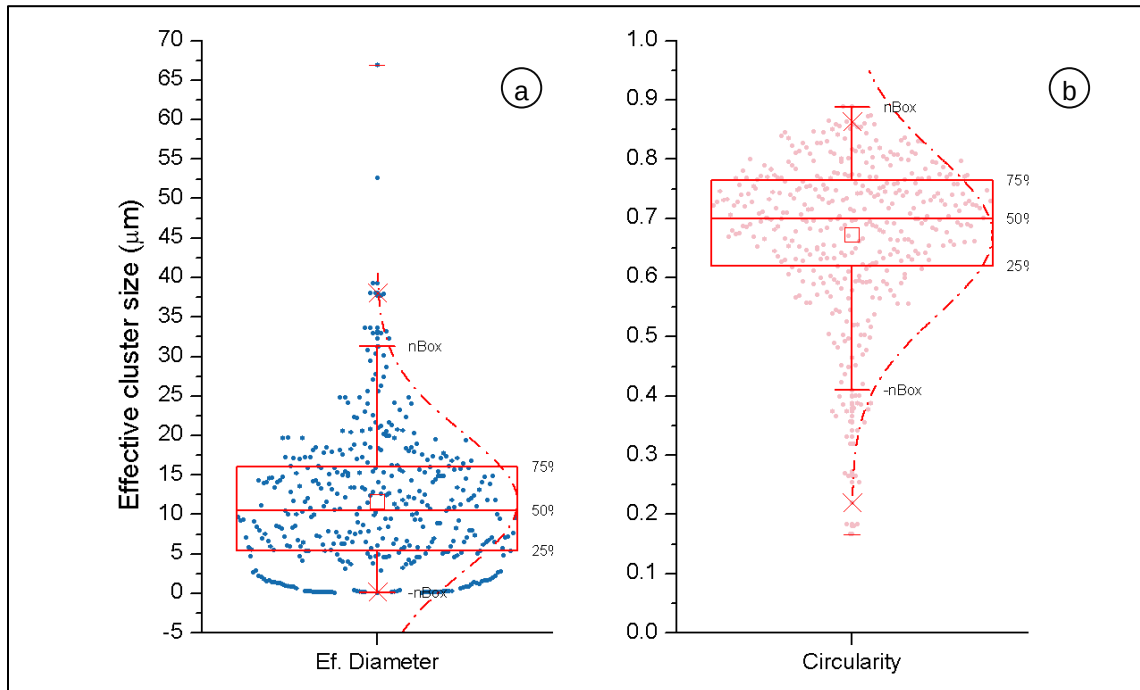


Figure 48. Size distribution of effective diameter and circularity of clusters in SUC sintered samples

The particle size distribution observed in Figure 48a is very wide, as evidenced by the large amount and by the concentration of points out of the box. This wide cluster size distribution is in accordance to the also suggested wide particle size distribution prior to sintering.

In the other side, the mean circularity ($\square$) of clusters is ~ 0.64 , indicating that the particles' consolidation tendency is evolving towards its lowest surface morphology: the spherical shape. Circularity points are also showed a wide spread dispersion of data, typical of the irregular homogenization and the early aggregation of the metal particles in the paste before getting to the sintering temperature.

The interpretation of the “outliers” (–) in these charts is apparent, i.e. the data beyond the 1% and 99% percentiles was taken only as indicators because the amount of data points plotted

per condition is not enough to establish a reliable statistical trend; therefore, additional data is necessary to satisfactorily differentiate an outlier from a dispersed data. From physical means we are still missing some micrographs aimed at qualifying a cluster size described as an outlier. With the lack of statistical data, an analysis of the errors is what was done in order to establish potential causes such as the determination of material contamination, test's parameters deviation, or any other cause for the mistake. Therefore the outliers were considered only as numerical indices which showed process trends.

❖ *Temperature effects*

The data for the temperature effect in the cluster size (see Figure 49) showed a response quite different from what was expected; the clusters were supposed to be always growing due to the advance of the sintering process (particles' aggregation). In Figure 49, the box plot for 400°C shows an average cluster size smaller than those those obtained at 300° and 500°C, which means an evident change in the structure due to the temperature level. Contrary to that, the box plots for the three temperatures tend to overlap implying similar statistical results of the three groups of conditions, or no significant (apparently) influence of temperature in the process.

A further analysis of the potential paths that the sintering mechanism may follow, suggests the possible dominance of the coarsening effect (see section 2.2) similar to that observed at lower temperatures. This coarsening effect dominates up until there is enough energy to activate the consolidation of the structure, i.e. the shrinkage. The results suggest that somewhere between 300° and 400°C, the sintering mechanism is suddenly changed from a coarsening mechanism to a densifying one, which led to a massive diffusion and a shrinkage effect producing the consolidation of the structure. This shrinkage is due to the pore elimination inside the clusters (see Figure 50).

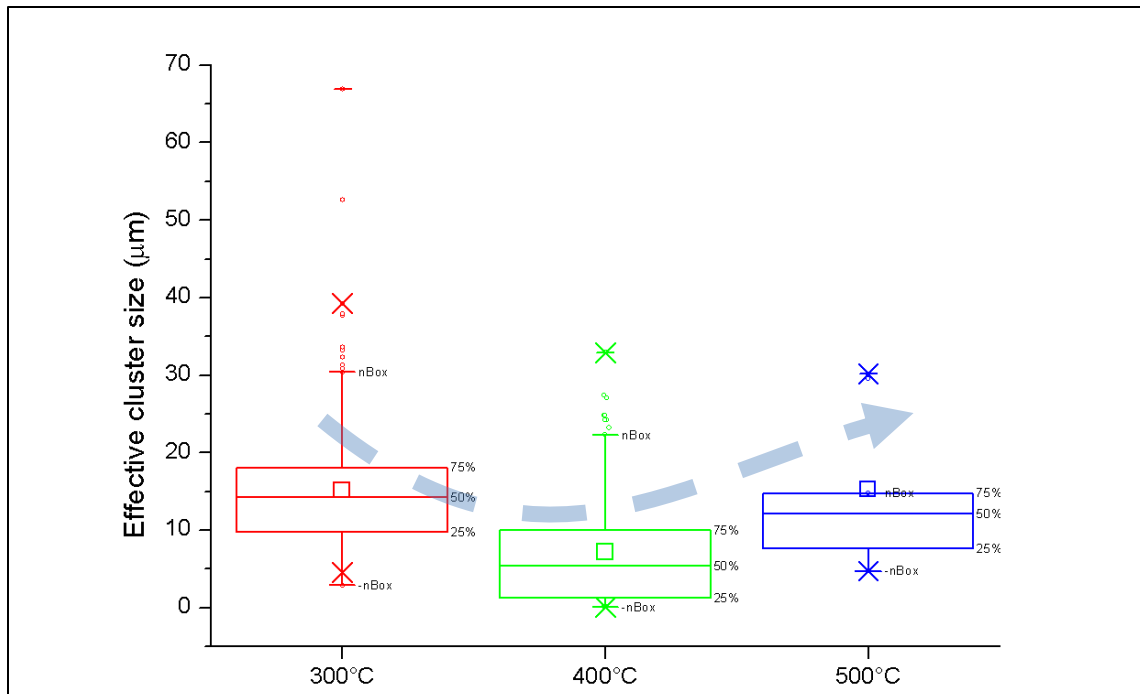


Figure 49. Effect of sintering temperature on the effective cluster size induced in SUC samples

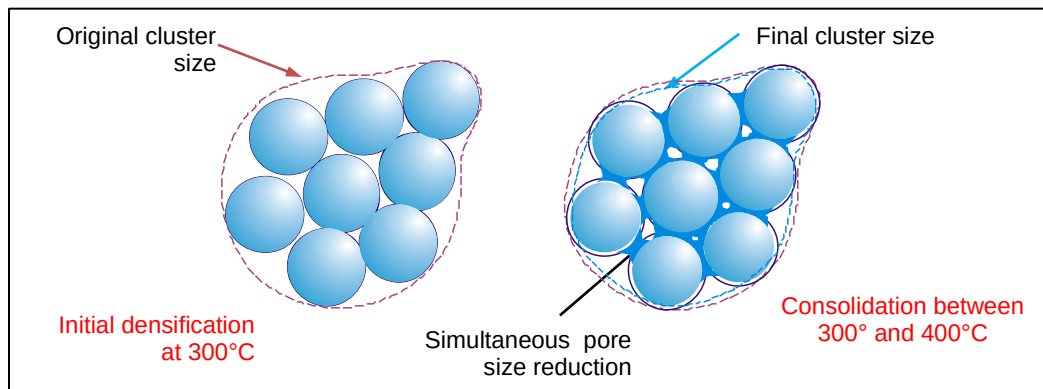


Figure 50. Activation of the cluster consolidation mechanism between 300° and 400°C

The energy required to activate the consolidation of the particles within a cluster is present, however it may not be enough to activate the consolidation between clusters yet.

Although the effect of the temperature may not be obvious on the basis of the comparison of the cluster's size across the selected temperature range, it proved to be a significant factor in determining the dominant mechanism for the progression of the sintering. It revealed a nonlinear

path for the transformations; thus establishing the sensitivity of the sintering progression on the processing temperature.

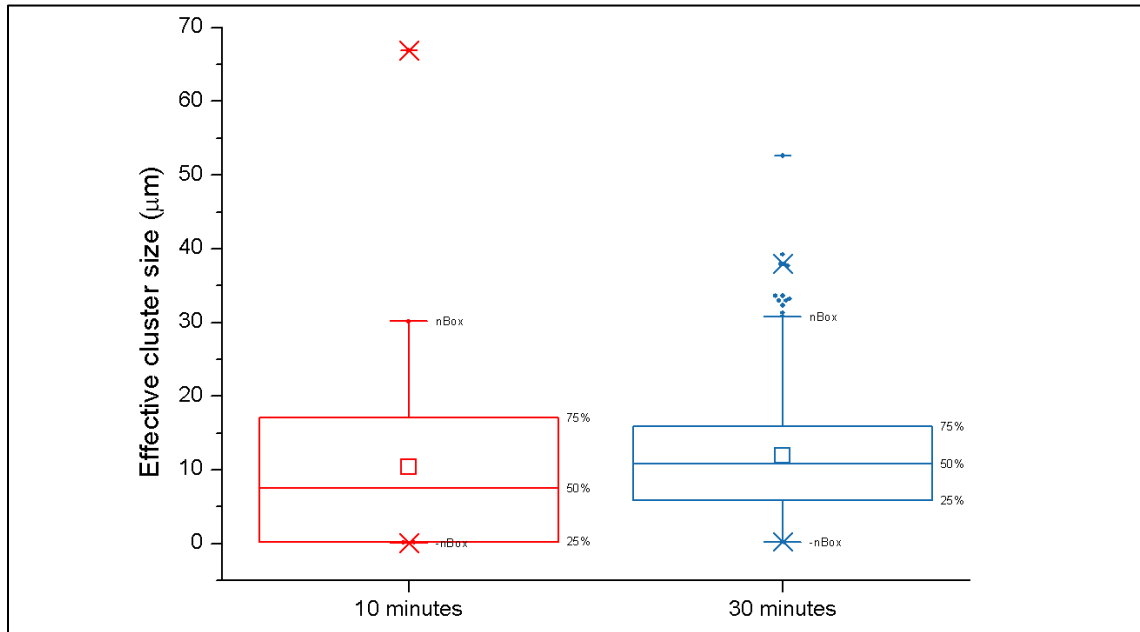


Figure 51. Effect of sintering time on the effective cluster size induced in SUC samples

❖ Time effects

The evaluation of the effect of the holding time at the sintering temperature on the cluster's size is presented in Figure 51. It shows a non-significant statistical difference as evidenced by the totally overlapped position of the box plots; hence the influence of the selected holding time range (10 and 30 minutes) on the progress of the sintering process can be neglected. This finding coincides with the results found in the DSC trials, where the time effect on the sintering progression was irrelevant.

A slight influence on the dispersion of data can be noticed; with wide distribution when samples lasted 10 minutes against a soft narrowing when they were exposed by 30 minutes to the

sintering temperature. Similarly, the consecution of more data will allow to attain reliable conclusion with this respect.

❖ *Environment effects*

Figure 52 revealed a significant influence of the sintering environment on the cluster growth due to progressive particle aggregation, as shown by the offset of the box plots. There, Argon atmosphere led to a significant growth of the clusters when compared with samples processed in air. The mechanism of this enlargement is not clear with the gathered data.

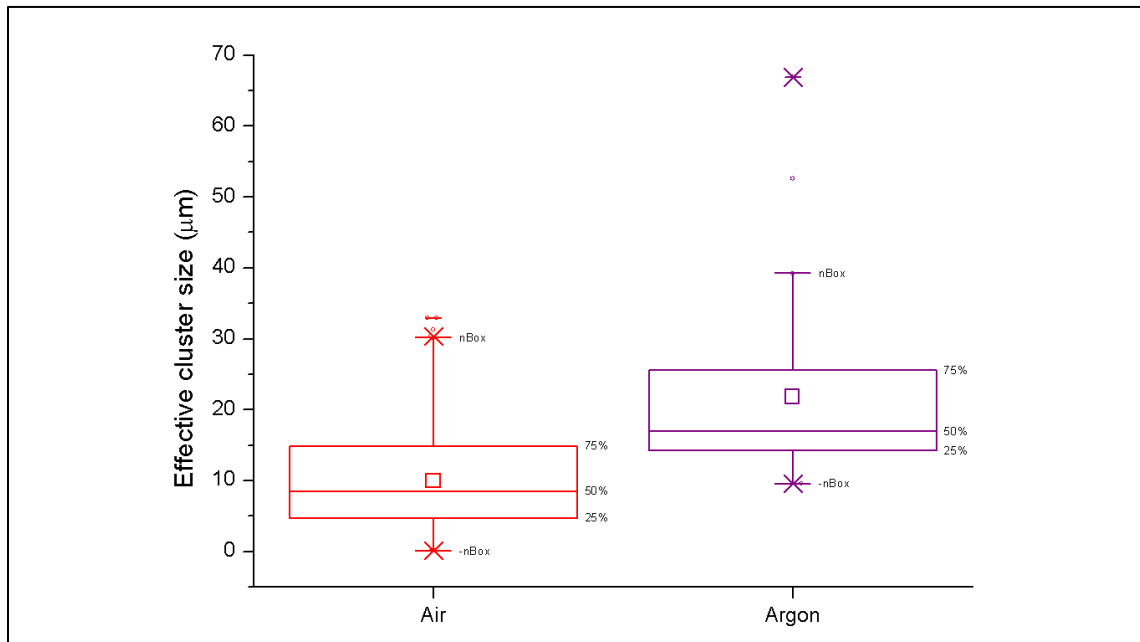


Figure 52. Effect of the sintering environment on the effective cluster size induced in SUC samples

The local effect of the environment affects the particles' surface, and such interaction might be influenced by several phenomena; two hypothesis have been suggested to find an explanation: the first is associated to the influence of the environment on reducing the surface tension of particles; thus, apparently enhancing the sintering between facing particles and

favoring the mass transport between those with a slight contact; therefore, the densification gets enhanced. The second proposed possibility is that a skin effect could be taking place at a certain temperature between 300° and 400°C promoting the argon gas absorption into the lattice, hence generating diminutive isolated pores and forming a sponge like structure causing the observed swelling.

These results deserve further experiments and analysis in order to validate the hypothesis that had been formulated or to reveal the real phenomenon.

6.7.3. *FUC samples: image analysis results*

The distinctive responses of the FUC (flaky uncoated) particles are presented next with the statistical support.

The qualitative analysis of the images taken from FUC samples showed a totally connected structure after sintering with a complete absence of clusters or discrete formations. The convoluted shape of the pores, which are clearly connected to each other, discloses that the sintering has definitely evolved from its first stage (neck growing) to densification leading to grain boundary motion (intermediate stage)³³, i.e. to a more mature stage where its evaluation can be assessed through the pore evolution measurement, rather than the previously used cluster metric, because they have already disappeared and have given pass to the above mentioned connected structure. The measurement of distinguishable features in these networks was similar to that used for cluster structures; that is, by means of isolated patterns assessment. The cluster structure was discrete and easy to quantify, but now the equivalent characteristic, i.e. the pores,

³³ See in section 2.5 the pertinent sintering theory.

became the key quantifiable trait. Based on the fact that the isolated features (pores) are to be measured, parameters such as equivalent diameter and circularity became the variable of interest which resulted in an indirect method to describe the evolution of the network structure. According to this, the measurements were performed to the pores and plotted in box plots. Results showing the effect of temperature, holding time, and processing environment on the sintering evolution are evaluated next.

Figure 53 presents the general results on the size distribution and circularity of pores in FUC samples after sintering. The mean of the effective pore size is $\sim 0.5 \mu\text{m}$ and it is one order smaller than the size of the formed clusters for SUC samples. This value of pore size represents the central trend of all data points. The chart shows a more concentrated data, i.e. less dispersed; again the consideration of the outliers is apparent and they are taken as indicators of behavior.

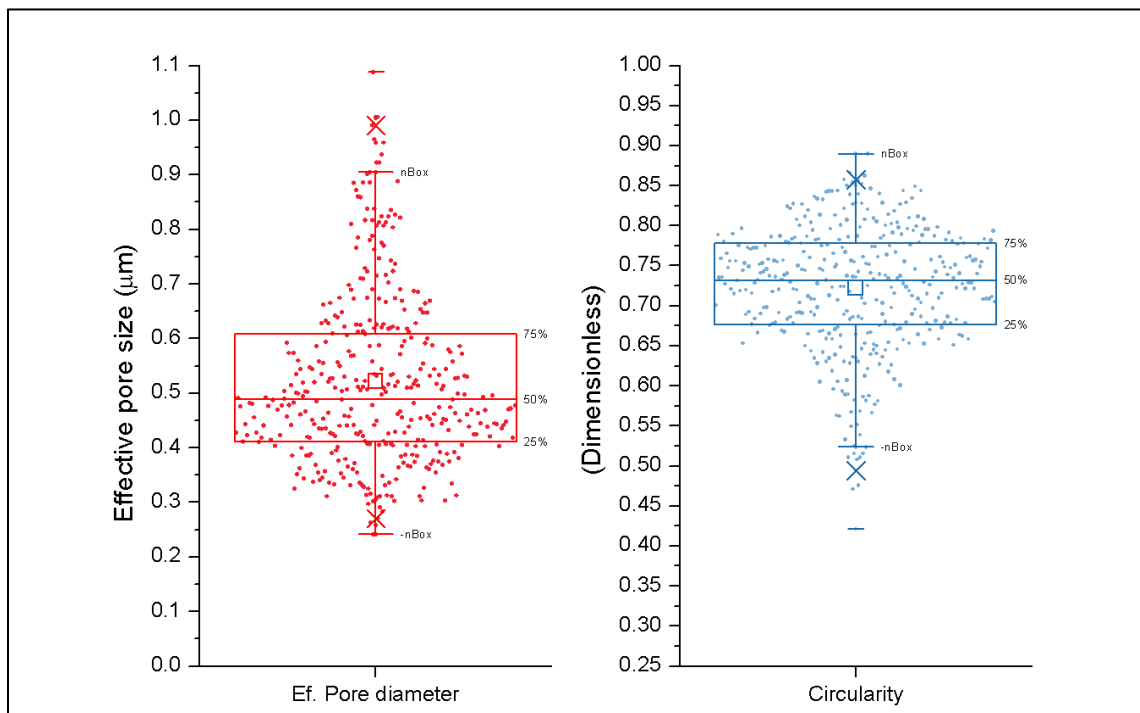


Figure 53. Size distribution of effective pore diameter and circularity of pores in FUC sintered samples

The dispersion of data is also significant in these results, which makes it necessary to add more measurements to attain significant numerical values about the variables affecting the process.

The mean of circularity is ~ 0.73 , which is higher than the circularity of the clusters of SUC particles (~ 0.65), reflecting an enhanced surface smoothing and more stable state of the structure after sintering. When clusters have high circularity and they lie together, the pores that they form tend not to have a high circularity; instead, their form may be circular but rough. Clusters turned into a connected web as they blend together until get despaired as structures; this gives a path for net transformations which promotes the sintering by reducing the amount of pores and their size. Afterwards, the pores tend to get isolated (which is characteristic of the third stage of sintering) by smoothing their boundaries and assuming a spherical shape, to later continue reducing their size (the final stage of sintering).

❖ *Temperature effects*

A equivalent tendency to the cluster measurement for SUC samples was observed with the measurement of the pore size and their dependence on temperature. The plotted results showed (see Figure 54) a general (apparent) rising trend of pore size with rising temperature. Nonetheless, an irregularity with sintering results was found when a higher pore size was observed with samples treated at 400°C . An explanation to this counterintuitive behavior may be suggested based on the sintering mechanism of the clusters in the SUC samples as already studied. First, a pore size swelling may suggest a contraction of the structure, which is coherent with the behavior observed in the cluster's size variation of the SUC samples at the same temperature level (400°C). Again, a massive diffusion gets activated at a critical point

somewhere between 300° and 400°C, shrinking the structure as it gets consolidated, therefore producing a pore expansion. The ongoing evolution of the sintering gives way to a subsequent pore size reduction. This is not a real rising behavior tendency, as it is shown in Figure 54; since the pore size swelling is present until the structure reaches a maximum absorbed energy level. Then, a densification process is activated, which promotes the pore size reduction through the mechanisms explained by the sintering theory (see section 2.5).

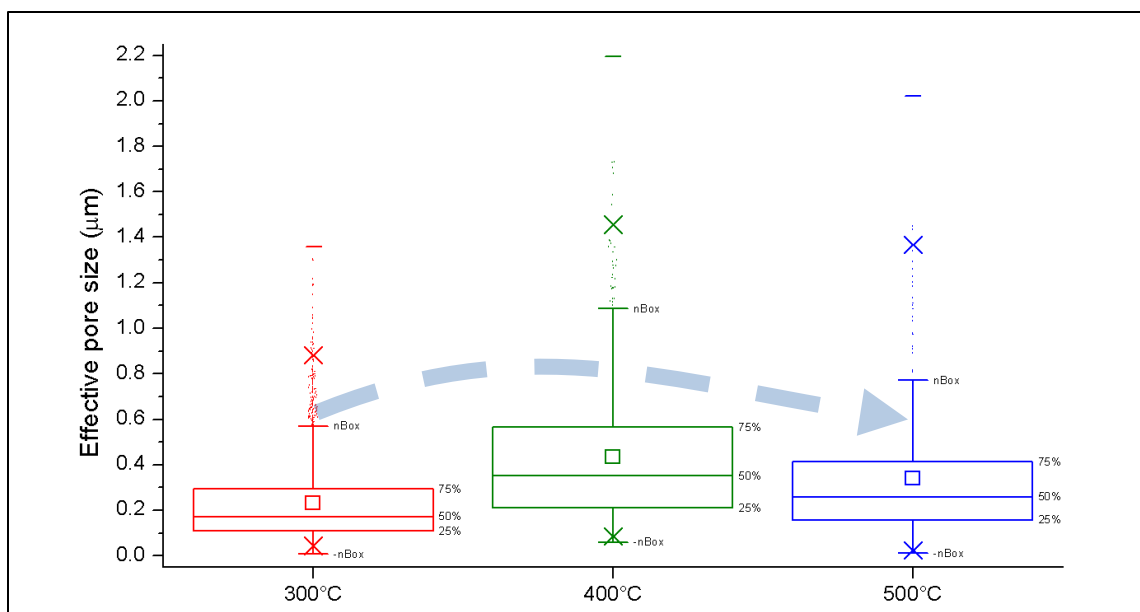


Figure 54. Effect of the sintering temperature on the effective pore size induced in FUC samples

The plots also showed a large data dispersion for all conditions, which may imply the need for more data points in order to extract a numerical indicator for the process.

❖ *Environment effects*

The evaluation of the pore size behavior with respect to the environmental conditions showed a decreasing trend; this data reflects a clear effect of the environment as given by the offset of the means and the difference in the dispersion of the box plots (see Figure 55). The

dispersion of data points in the box chart of Argon suggests a noticeable enhancing of the homogeneity in the sintering results with such narrow distribution.

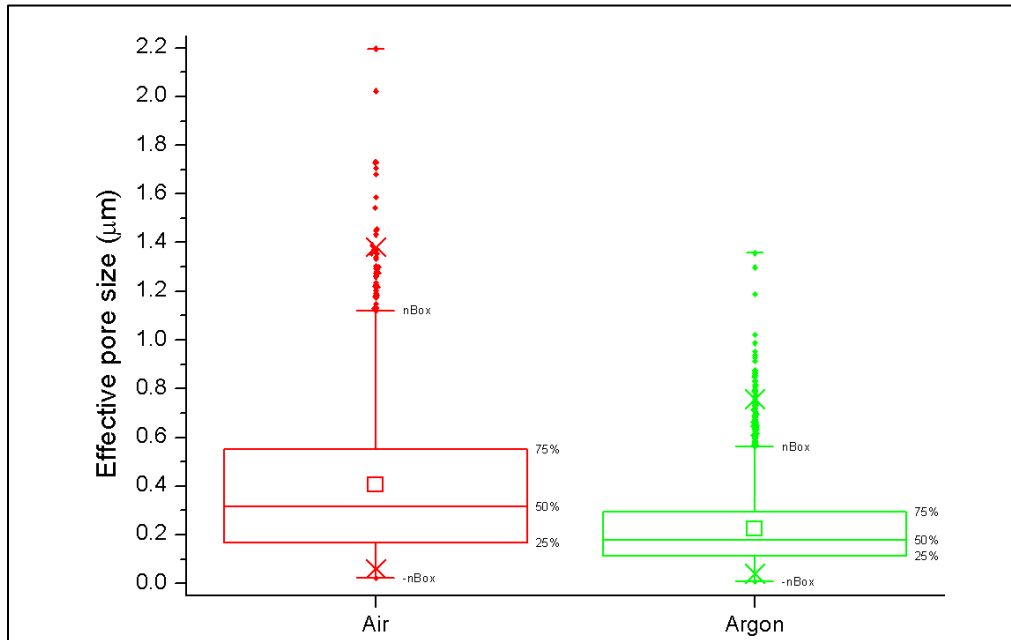


Figure 55. Environment effect in the size distribution of effective diameter of FUC particles

The pore size contraction in the Argon atmosphere means a structural consolidation as it was clearly appreciable with the box that was analyzed for the temperature effects in FUC samples. This behavior is coherent with that presented in SUC samples processed under the same conditions; i.e. an important structural improvement of sintering resulted from the sintering in Argon atmosphere.

❖ *Time effects*

The box plots presented in Figure 56 showed a quite similar behavior; their averages and medians are too close to each other, therefore no statistical evidence to prove a cause and effect can be extracted which means that the time effect is negligible in the evaluated range. This in

accordance with the findings from the SUC sintered particles evaluated with respect of the sintering holding time.

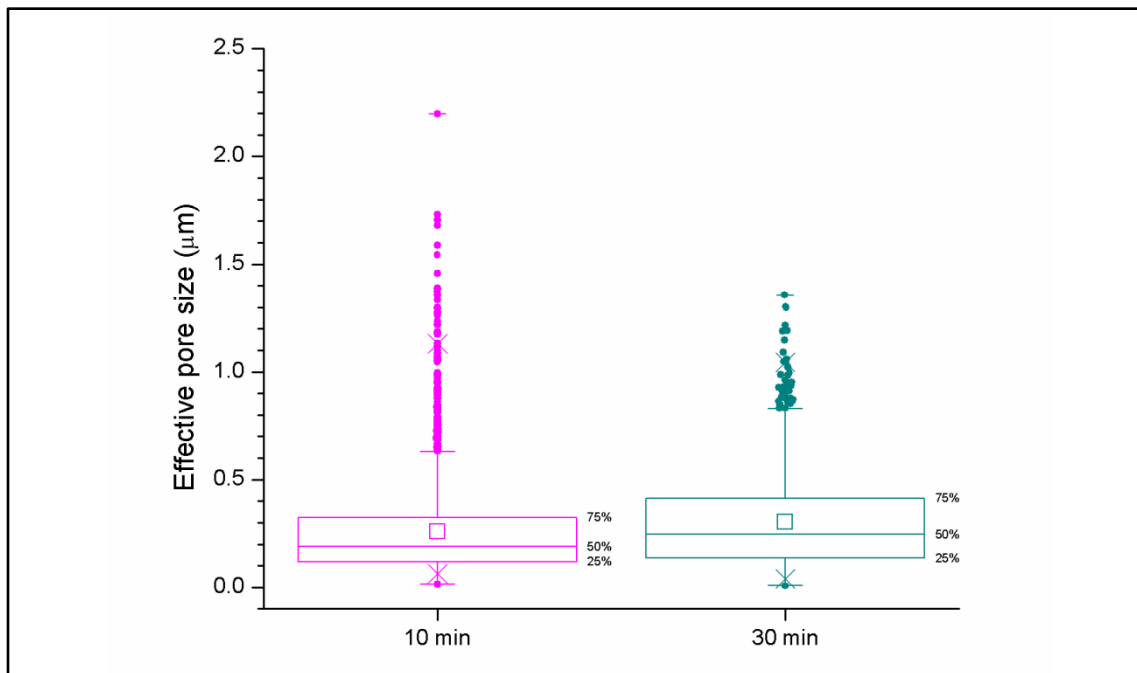


Figure 56. Effect of sintering time on the effective pore size on FUC particles

6.7.4. SOC samples: image analysis results

The SOC (spherical oleic coated) particles and their particular responses are presented next along with the statistical analysis.

Figure 57 presents the results of the effective diameter and circularity of pores in sintered SOC samples. The dispersion data for the pore size results good, and when compared with the results of FUC sintered samples (see Figure 53), a noticeable improve in the homogeneity of effective pore size are indicative of the excellent results obtained with SOC particles. This observation ratifies the results obtained through the qualitative analysis in Table 9.

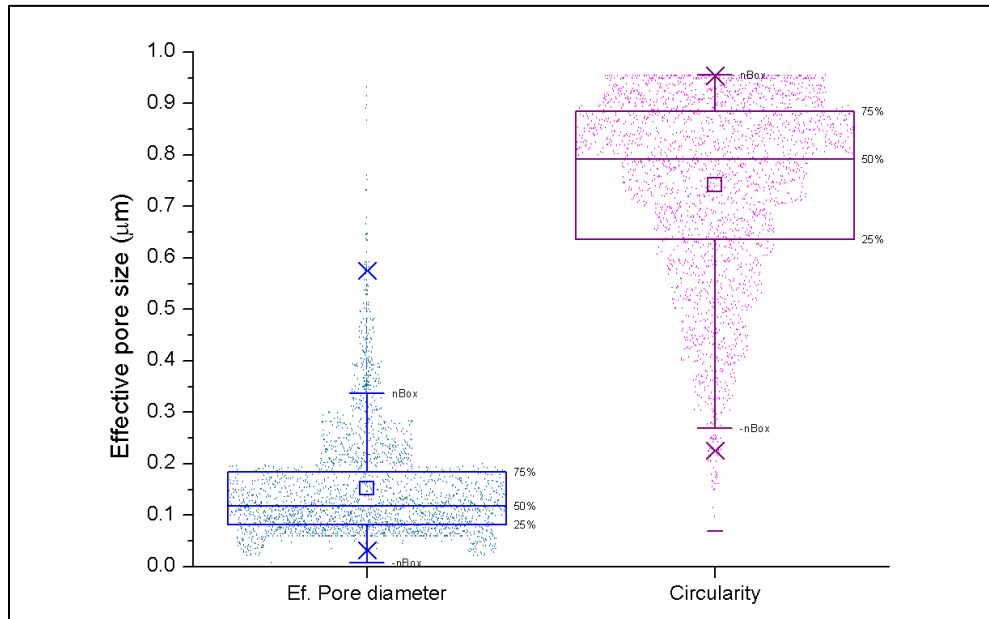


Figure 57. Size distribution the effective diameter and circularity of pores in SOC particles.

The mean circularity index is ~ 0.75 which is better than the previous results in FUC samples; this, combined with the higher homogeneity in the effective pore size supposes a better consolidation of the material. The already presented qualitative evaluation results are now confirmed with these quantitative findings.

❖ *Time effects*

The effect of holding time in sintering development proved not to be significant according to the results shown in Figure 58 for SOC sintered samples. This could be attributed to the small window in the holding time range used for the experimental settings.

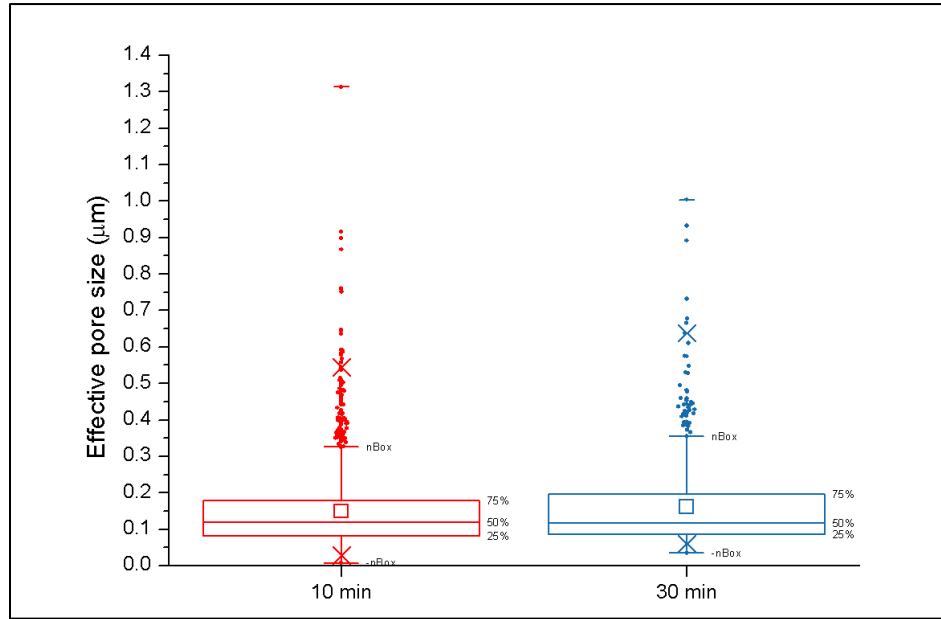


Figure 58. Effect of sintering time on the effective pore size in SOC samples.

6.7.5. Summary of image processing analysis

A significant dispersion of the data on cluster size and pore size distribution was prevalent in all results, however valuable insights were revealed during the analysis, suggesting a clear path for further investigation. It is worth noting that due to the complexity of the interactions of the process parameters during the empirical trials, it was not possible to extract specific numerical information, but the results provided a “semi-qualitative” description of the mechanisms.

Sintering temperature and processing environment proved to be quite influencing in the sintering development of the SUC and FUC samples, triggering a massive densification/consolidation between 300° and 400°C to later evolve towards a pore size reduction. Contrary to that, the holding time effect was not significant (for the evaluated time range) in both SUC and FUC samples. The lack of evidence of the effect of holding time was

also confirmed by the previous DSC results (see section 6.1) where holding time effects in the heat curves were not evident.

The Argon atmosphere resulted in a significant increase of the cluster size in SUC samples, as well as a pore size reduction (which is equivalent) of FUC particles when it was used for processing. These two indicators: pore size and cluster size are the key elements for the assessment of the sintering mechanisms; hence, argon environment proved to be pivotal for the evolution of the pressureless sintering mechanism.

These results, combined with the findings from the DSC and XRD in addition to the qualitative analysis offered an alternative for enhancing the results on the sintering of Ag nanoparticles by combining properties such as coating layer, process environment, heating rate, and the geometry of the precursor particles.

There were good results despite of the enlargement of the structures by the aggregation prior to sintering which may become a drawback only when it gets uncontrollable, hence producing adverse responses such as fragmentation, non-consolidated structures, and non-homogeneous structures. Therefore, it is preferred to know the nominal size of the raw particles and to try to control their aggregation; however, it is not imperative to know the exact size distribution of particles, especially in highly concentrated pastes, i.e. for the projected application conditions.

The aforementioned indices proved to provide enough information to safely propose the enhancement of the process in an attempt to further apply it in die attach solutions.

7. CONCLUSIONS

DSC results revealed critical reactions occurring during the sintering process, where the observed exothermic peaks confirmed the recrystallization and grain growth of the internal structures, which is indeed the basis for the sintering mechanism. These thermal results, together with the image analysis findings are proofs of the undeniable effect of temperature on driving the sintering evolution mechanism. The desired processing temperature of 300°C was confirmed as sufficient to partially activate the process. The stability of the resulting structure as tested by repeated thermal cycles showed the benefits of the irreversibility of this pressureless sintering process.

XRD spectroscopy confirmed the absence of pre-existing or the generation of contaminants (oxides) during the process; it also confirmed the integrity of the base material as silver, highlighting its capabilities as a noble metal for the pressureless sintering.

The image analysis was definitive in demonstrating the structural state of the material and revealed the main features associated with sintering evolution: clusters and pores; their size and shape prone to be relevant indicators of the sintering development. However, it was demonstrated that their formation is very sensitive to the shape and size of the precursor material.

The stereological analysis revealed specific details on the development of the sintering mechanism. An important stereological finding, which opened up area for further research, was the evident influence of the argon environment in enlarging clusters and reducing pores which is fundamental mechanism towards the completion of the sintering process.

The qualitative analysis of the physical characteristics of the sintered samples provided crucial information in terms of macroscopic response which was not necessarily assessed during this investigation, but with no doubt, was inferred by the experimental trials that focused at smaller length scales. The solid compaction obtained with the spherical-oleic_acid-coated (SOC) nanoparticles was significant, that together with the excellent consolidation of the spherical-uncoated (SUC) nanoparticles into continuous bodies suggests that a combination these two could result in a great enhancement of the actual process. Thereby, the pressureless sintering of nanoparticles can be significantly improved by the combination of particle types and consequently, their sintering mechanisms.

It is believed that capped silver nanoparticles (smaller than 35nm) will provide excellent consolidation to the final sintered material, while their coupling with uncoated particles (with sizes less than 80nm) will ease the conforming of all particulate as a whole compact body, thus avoiding the undesirable cracking. It is suggested that small particles (as SOC) will be a very active agent to the sintering, while the biggest particles (SUC) will provide the structural conformation and they will active in the sintering development, consuming less energy and off course, easing the energy destination to the smaller particles.

Similar to the behavior of cement and sand, it is expected that small particles will get accommodated in the interstitial spaces between the bigger particles, acting as a blender during the sintering process (see Figure 59). The quantity of silver in the paste with this configuration can remain the same, while reducing the content of oleic acid, then reducing sintering at low temperatures and optimizing the process at the sintering temperatures. The expected result must be a homogeneous, consolidated, and well conformed material, where the mixture can exert a key action in enhancing the mechanism for the pressureless sintering of silver nanoparticles.

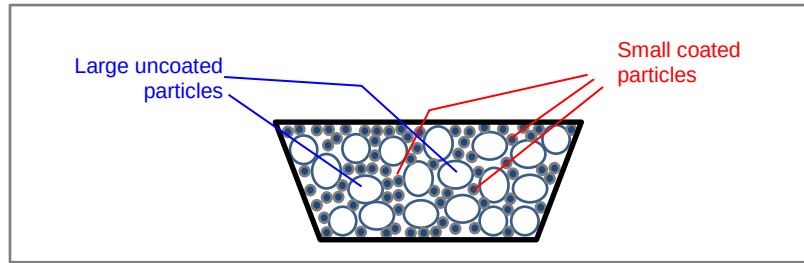


Figure 59. Ag Particle mixture: small and big particles, uncoated and coated particles

All our findings indicated that the evaluated size, shape, surface, and environmental conditions of the nanoparticles are critical factors for the sintering mechanism of Ag nanoparticles.

8. CONTRIBUTION

- * Development of an analytic method capable of linking sintering critical control parameters with structural features of interest across different length scales into a single indicator that can be used to study the progression of the process.

- * This work has enabled a tool capable of studying the evolution of a pressureless sintering mechanism from the nano to the macroscale on the basis of a stereological analysis.

9. RECOMENDATIONS

Particle size distribution has been found to be critical, then mixing of two populations is recommended so that the sintering mechanisms could be optimized. However, particle sizes above 200nm are not recommended due to agglomeration problems.

The range of particle sizes and their proportions in the mixture will have a direct effect on the processing temperature. Processing environment proved to be pivotal, therefore testing with other gases is highly recommended. The combination of particle sizes together with the study of processing atmosphere will allow the optimization of the process temperature.

The micrographical inspection can be enhanced by using as a reference the present micrographs, because the classical metallographic techniques may generate artifacts. Working with backscattering methods will reduce textures and the aliasing, and scales up to 10 μm must be evaluated.

Engineering tests such as thermal conductivity, electric conductivity, shear strength, and thermal stresses will be fundamental in measuring of the functionality of this material as a die attach. Shear strength, and thermal stresses may be affected by the internal generation of gases during the sintering process, therefore special attention to the interfaces has to be taken in order to obtain real and conclusive results.

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APENDIX

Appendix I . Commonly used materials for various package elements

Package	Element Materials
Chip carriers and substrates	Ceramic: alumina, beryllia, silicon carbide, aluminum nitride, silicon nitride, forsterite
Semiconductor die	Metal: Molybdenum, copper-tungsten, tungsten, Kovar, stainless steel Silicon, germanium, silicon carbide, gallium arsenide, cadmium sulfide, indium antimonide, lead sulfide, II–V and II–VI compounds
Die attach and adhesive	Silicone, polyurethane, acrylic, epoxy Novolac, epoxy phenolic, epoxy polyamide, solder
Wires for bonding	Gold and aluminum
Leads	Kovar
Lead seals	Glass
Lids	Same as case/chip carrier materials
Lid seal	Welding, brazing, and solder materials
Encapsulants	Silicones, epoxies, polyimides, polyamides, polyurethanes, fluorocarbons, acrylics, diallyl phthalate, polyvinyl chloride, parylene

Appendix II. Solder alloys, composition and states

Temperature (°C)			Elements (%)								
Solidus	Liquidus	Eutectic	Pb	Sn	Ag	Ln	Sb	Bi	Cd	Au	Zn
—	—	93	—	42	—	44	—	—	14	—	—
—	—	95	32	15.5	—	—	—	52.5	—	—	—
—	—	117	—	48	—	52	—	—	—	—	—
118	125	—	—	50	—	50	—	—	—	—	—
—	—	125	43.5	—	—	—	—	56.5	—	—	—
—	—	125	9.6	15	—	70	—	—	5.4	—	—
—	—	138	—	—	—	42	—	58	—	—	—
—	—	139	—	43	—	—	—	57	—	—	—
—	—	143	—	—	3	97	—	—	—	—	—
—	—	145	30.6	51.2	—	—	—	—	18.2	—	—
155	149	—	15	—	5	80	—	—	—	—	—
—	—	146	32	50	—	—	—	—	18	—	—
—	—	162	18	70	—	12	—	—	—	—	—
144	163	—	43	43	—	—	—	14	—	—	—
156	165	—	25	—	—	75	—	—	—	—	—
160	174	—	30	—	—	70	—	—	—	—	—
—	—	177	—	67.8	—	—	—	—	32.2	—	—
—	—	179	36.1	62.5	1.4	—	—	—	—	—	—
—	—	183	38.1	61.9	—	—	—	—	—	—	—
183	186	—	35	65	—	—	—	—	—	—	—
179	189	—	36	62	2	—	—	—	—	—	—
183	190	—	40	60	—	—	—	—	—	—	—
183	192	—	30	70	—	—	—	—	—	—	—
183	195	—	25	75	—	—	—	—	—	—	—
183	195	—	42	58	—	—	—	—	—	—	—
—	—	198	—	91	—	—	—	—	—	—	9
183	202	—	20	80	—	—	—	—	—	—	—
183	203	—	45	55	—	—	—	—	—	—	—
180	209	—	50	—	—	50	—	—	—	—	—
183	209	—	15	85	—	—	—	—	—	—	—
183	214	—	50	50	—	—	—	—	—	—	—
183	215	—	10	90	—	—	—	—	—	—	—
—	—	215	85	—	15	—	—	—	—	—	—
183	218	—	48	52	—	—	—	—	—	—	—
—	—	221	—	96.5	3.5	—	—	—	—	—	—
183	224	—	5	95	—	—	—	—	—	—	—
183	225	—	55	45	—	—	—	—	—	—	—
179	227	—	35.5	61.5	3	—	—	—	—	—	—
221	229	—	—	96	4	—	—	—	—	—	—
183	238	—	60	40	—	—	—	—	—	—	—
233	240	—	—	95	—	—	5	—	—	—	—
183	242	—	62	38	—	—	—	—	—	—	—
221	245	—	—	95	5	—	—	—	—	—	—

Appendix III. Solder alloys, composition and states (continuation)

Temperature (°C)			Elements (%)								
Solidus	Liquidus	Eutectic	Pb	Sn	Ag	Ln	Sb	Bi	Cd	Au	Zn
179	246	—	36	60	4	—	—	—	—	—	—
—	—	246	89.5	—	—	—	10.5	—	—	—	—
183	247	—	65	35	—	—	—	—	—	—	—
—	—	248	82.6	—	—	—	—	—	17.4	—	—
—	—	252	88.9	—	—	—	11.1	—	—	—	—
183	258	—	70	30	—	—	—	—	—	—	—
250	264	—	75	—	—	25	—	—	—	—	—
183	268	—	75	25	—	—	—	—	—	—	—
—	—	280	—	20	—	—	—	—	—	80	—
183	280	—	80	20	—	—	—	—	—	—	—
225	290	—	85	15	—	—	—	—	—	—	—
268	299	—	88	10	2	—	—	—	—	—	—
296	301	—	93.5	5	1.5	—	—	—	—	—	—
268	302	—	90	10	—	—	—	—	—	—	—
—	—	304	97.5	—	2.5	—	—	—	—	—	—
—	—	309	97.5	1	1.5	—	—	—	—	—	—
301	314	—	95	5	—	—	—	—	—	—	—
—	—	318	99.5	—	—	—	—	—	—	—	0.5
316	322	—	98	2	—	—	—	—	—	—	—
304	365	—	94.5	—	5.5	—	—	—	—	—	—

Appendix IV. Thermomechanical properties of packaging materials

Material	CTE	Thermal Conductivity	Modulus of Elasticity
	(ppm/°C)	@25°C (W/m·K)	(GPa)
Ceramics			
Alumina 92%	7.2	17	280
Alumina 96%	6.3	21	303
Alumina 99.9%	7.4	30	370
Aluminum nitride	4.2	170	350
Beryllium oxide	6.4	248	345
LTCC	4.5–8.0	2.0–4.4	152
Metals			
Aluminum	23.6	237	68
AlSiC (37% SiC)	10.9	170	167
AlSiC (55% SiC)	10.16	181.4	167
AlSiC (63% SiC)	8.37	180	188
Kovar®*	5.5	16.5	137.9
Copper–tungsten 80:20	8.3	185	
Copper–tungsten 85:15	7.2	180	274
Copper–tungsten 90:10	6.5	170	306
OFHC copper	16.8	401	117
Dispersion-strengthened copper	16.6	365	
Molybdenum	5.35	138	330
Cu–Mo–Cu (1:6:1) clad	6.4	233	
CuMo (15 Cu, 85 Mo)	6.7	160	239
Cu–Invar–Cu (1:3:1) clad	6.5	174 x and y 24.8 z	
Silva®*	6.6–7.0	110–153	110
Aluminum–graphite	7.5	190	
Aluminum–silicon	7–23	120–180	45
Gases			
Air	na	0.0024	na
Nitrogen	na	0.0024	na
Semiconductors			
Silicon	2.49	150	112.4
Silicon carbide	4.5	155	450
Gallium arsenide	5.4	45	85.9
Indium phosphide	4.6	97	

Appendix V. Functional purposes of metallization layers

UBM	Evaporated (typical of C4)	Plating (two processes)	Solder Paste (typ. FCT)	Electroless nickel
Adhesion layer	CR	(1) TiW or (2) Cr/Cu	Al	Ni
Solder diffusion layer	Phased	(1) Cu stud/minibump	Ni	Ni
	Cr-Cu	(2) Cr-Cu		
Solder wettable layer	Cu	(1) Cu (2) Cu	Cu	Au
Oxide prevention	Au	Au	Cu	Au
Suitability for 63Sn/Pb	No	(1) Poor (2) No	Yes	Yes
Use with Probed Wafers	No	No	Yes	Mixed

Appendix VI. Kinetic equations of sintering mechanisms [29]

Sintering mechanism	Neck growth	Shrinkage
Surface diffusion (Kuczynski)	$\left(\frac{x}{a}\right)^7 = \left(\frac{56\gamma_s V_m \delta D_s}{kT r^4}\right) \cdot t$	N/A
Evaporating condensation (Kuczynski)	$\left(\frac{x}{a}\right)^3 = \left(\frac{3\sqrt{\pi}\alpha\gamma_s M^{\frac{3}{2}} p_o}{\sqrt{2} R^{\frac{3}{2}} T^{\frac{3}{2}} d^2 r^2}\right) \cdot t$	N/A
Volume diffusion (Kingery)	$\left(\frac{x}{a}\right)^5 = \left(\frac{80\gamma V_m D_\alpha}{kT r^3}\right) \cdot t$	$\left(\frac{\Delta L}{L_o}\right)^{\frac{5}{2}} = \left(\frac{20\gamma V_m D_\alpha}{\sqrt{2} kT r^3}\right) \cdot t$
Grain boundary diffusion (Coble)	$\left(\frac{x}{a}\right)^6 = \left(\frac{192\gamma V_m \delta D_b}{kT r^4}\right) \cdot t$	$\left(\frac{\Delta L}{L_o}\right)^3 = \left(\frac{3\gamma V_m \delta D_b}{kT r^4}\right) \cdot t$
Viscous flow (Frenkel)	$\left(\frac{x}{a}\right)^2 = \left(\frac{3\gamma}{2\pi\eta r}\right) \cdot t$	$\left(\frac{\Delta L}{L_o}\right) = \left(\frac{9\gamma}{4\eta r}\right) \cdot t$

In the table variables mean:

- k : Boltzmann constant
- D : Diffusion coefficient
- V_m : Molar volume
- η : Viscosity
- α : solid phase
- δ : neck thickness
- r : particle size

Appendix VII. Comparison of properties of commercial solders with respect to silver sintered materials
[12]

	Eutectic lead-tin solder	Lead-free solder	Eutectic gold-tin solder	Conductive Epoxy	Nanosilver paste
Bonding mechanism	Liquidus reflow	Liquidus reflow	Liquidus reflow	Epoxy curing	Sintering/solidus interdiffusion
Peak process temperature	214°C	260°C	320°C	~150°C	280-300°C
Composition	Pb37Sn63	Sn96.5Ag3.5	Au80Sn20	Silver filler and organic resin and hardener	Pure silver (>99.8 wt.%)
Maximum use temperature	<180°C	<220°C	<280°C	<150°C	<960°C
Electrical conductivity	0.69×10 ⁵ (10e5-cm) ⁻¹	0.82×10 ⁵ (10e5-cm) ⁻¹	0.62×10 ⁵ (10e5-cm) ⁻¹	~0.1×10 ⁵ (10e5-cm) ⁻¹	2.6×10 ⁵ (10e5-cm) ⁻¹
Thermal conductivity	51 (W/K-m)	60 (W/K-m)	58 (W/K-m)	~0.1 (W/K-m)	240 (W/K-m)
Coefficient of thermal expansion	25 (PPM/°C)	22 (PPM/°C)	16 (PPM/°C)	~25 (PPM/°C)	19 (PPM/°C)
Elastic modulus	16 GPa	26 GPa	68 GPa	<1 GPa	10 GPa
Yield Strength	27 MPa	22.5	N/A	N/A	43 MPa
Tensile strength	27 MPa	52 MPa	275 MPa	~10 MPa	43 MPa

Appendix VIII. Schedule of sintering testes of uncoated silver nanoparticles

Type	Class	Rdm	Temp.	Time	Environm.
Flaky	1	8	300	10	argon
Flaky	2	19	300	10	argon
Flaky	3	15	300	30	argon
Flaky	4	11	300	30	argon
Flaky	5	12	400	10	argon
Flaky	6	23	400	10	argon
Flaky	7	2	400	30	argon
Flaky	8	24	400	30	argon
Flaky	9	3	500	10	argon
Flaky	10	20	500	10	argon
Flaky	11	6	500	30	argon
Flaky	12	10	500	30	argon
Spherical	13	21	300	10	argon
Spherical	14	9	300	10	argon
Spherical	15	18	300	30	argon
Spherical	16	14	300	30	argon
Spherical	17	7	400	10	argon
Spherical	18	13	400	10	argon
Spherical	19	5	400	30	argon
Spherical	20	17	400	30	argon
Spherical	21	4	500	10	argon
Spherical	22	16	500	10	argon
Spherical	23	22	500	30	argon
Spherical	24	1	500	30	argon
Spherical	25	10	300	10	oxygen
Spherical	26	9	400	30	oxygen
Spherical	27	26	200	10	argon
Flaky	27	30	250	30	argon
Spherical	28	27	250	30	argon
Spherical	28	28	200	30	argon
Flaky	29	29	250	10	argon
Flaky	29	31	200	10	argon
Spherical	30	25	250	10	argon
Flaky	30	32	200	30	argon
Flaky	37	17	300	10	oxygen
Flaky	38	33	300	10	oxygen

Type	Class	Rdm	Temp.	Time	Environm.
Flaky	39	3	300	10	oxygen
Flaky	40	32	300	30	oxygen
Flaky	41	23	300	30	oxygen
Flaky	42	21	300	30	oxygen
Flaky	43	25	400	10	oxygen
Flaky	44	27	400	10	oxygen
Flaky	45	14	400	10	oxygen
Flaky	46	13	400	30	oxygen
Flaky	47	34	400	30	oxygen
Flaky	48	26	400	30	oxygen
Flaky	49	18	500	10	oxygen
Flaky	50	29	500	10	oxygen
Flaky	51	4	500	10	oxygen
Flaky	52	5	500	30	oxygen
Flaky	53	2	500	30	oxygen
Flaky	54	19	500	30	oxygen
Spherical	55	9	300	10	oxygen
Spherical	56	20	300	10	oxygen
Spherical	58	31	300	30	oxygen
Spherical	59	11	300	30	oxygen
Spherical	60	16	300	30	oxygen
Spherical	61	28	400	10	oxygen
Spherical	62	10	400	10	oxygen
Spherical	63	24	400	10	oxygen
Spherical	65	1	400	30	oxygen
Spherical	66	30	400	30	oxygen
Spherical	67	15	500	10	oxygen
Spherical	68	8	500	10	oxygen
Spherical	69	6	500	10	oxygen
Spherical	70	22	500	30	oxygen
Spherical	71	7	500	30	oxygen
Spherical	72	12	500	30	oxygen

Appendix IX. Schedule of sintering testes of coated silver nanoparticles

Class	Run	Temp.	Time
1	5	200	10
2	8	200	10
3	14	200	10
4	10	200	30
5	19	200	30
6	24	200	30
7	16	250	10
8	20	250	10
9	23	250	10
10	9	250	30
11	22	250	30
12	25	250	30
13	3	300	10
14	7	300	10
15	17	300	10
16	2	300	30
17	12	300	30
18	18	300	30
19	13	400	10
20	21	400	10
21	1	400	30
22	26	400	30
23	4	500	10
24	15	500	10
25	6	500	30
26	11	500	30