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Master's Degree in Energy and Nuclear Engineering

Master's Degree Thesis



**Development of glass-ceramic sealing
materials and deposition techniques
for Oxygen Transport Membranes
integration onto metal supports**

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Abstract

The ongoing energy transition requires a shift away from fossil fuel combustion toward cleaner, more efficient industrial processes capable of supporting decarbonization. Within this context, pure oxygen plays a surprisingly central role, enabling technologies such as oxy-fuel combustion, gasification, and green hydrogen production, all of which contribute to improving energy efficiency and facilitating carbon capture. While established oxygen production methods such as cryogenic air separation and pressure swing adsorption remain dominant, Oxygen Transport Membranes (OTMs) are emerging as a promising alternative, offering continuous, high-purity oxygen separation with the potential for direct thermal integration into high-temperature industrial processes. OTMs are dense ceramic membranes made of mixed ionic-electronic conducting (MIEC) materials, which transport oxygen ions through the lattice via an oxygen partial pressure gradient, typically operating in the range of 800-1000°C. To be deployed industrially, OTMs must be integrated into modules consisting of single repeating units, where the membrane is joined to a metal support through a glass-ceramic sealant layer. This joint is a critical component of the module, as it must provide long-term gas tightness, possess a coefficient of thermal expansion (CTE) compatible with both the membrane and the metal support, and remain chemically and mechanically stable under prolonged exposure to the harsh working conditions of the device.

The objective of this thesis was to further optimize the joining process between OTMs and metal supports through the development of a suitable glass-ceramic sealant and its deposition technique, building upon previous work carried out at Politecnico di Torino in collaboration with RSE S.p.A. Specifically, the work aimed to refine the paste formulation and printing parameters used for robocasting, to further develop the thermal treatment curve applied during the joining process, and to explore tape casting as an alternative deposition method. In addition to LSCF single-phase membranes previously joined to Inconel 625 metal supports, a newly developed dual-phase membrane, 70CGO-30STF82, and Crofer 22 APU metal supports were introduced and studied as potential alternatives.

To meet these objectives, a Ba-based borosilicate glass, GC2, was prepared, milled, and sieved into a powder with particle sizes below 25 μm , with its properties verified through particle size analysis and Differential Scanning Calorimetry (DSC). For robocasting, a GC2-based paste was formulated and characterized rheologically through flow sweep and three-interval thixotropy tests (3ITT), leading to adjustments in the solid load, reduced from 82.5% to 80%, and in the printing parameters, with the print speed increased from 2 mm/s to 10 mm/s, in order to improve the paste's shear-thinning behavior and extrudability. For tape casting, a separate slurry formulation was developed, and a dedicated thermal treatment curve was designed based on Thermogravimetric Analysis (TGA) results performed on a previously prepared tape. Following deposition, samples were subjected to a thermal treatment procedure involving multiple dwell steps for the controlled evaporation of organic additives and a final dwell during cooling to promote the growth of crystalline phases within the glass-ceramic. The quality of the resulting joints was then assessed through X-ray computed tomography (CT) scanning and Scanning Electron Microscopy (SEM), focusing on the detection of cracks and pores.

Throughout the thesis work, six batches of GC2 glass were produced and seventeen samples were prepared, of which three were sent to RSE for non-destructive leakage and thermal aging testing. Samples produced via robocasting exhibited good adhesion to both the membrane and the metal support, although the formation of pores and occasional cracks remained a persistent issue for many samples, partly attributed to inconsistencies in the manual placement of weights used to apply pressure during joining. Following the adjustment of the printing parameters and the thermal treatment curve, porosity and crack formation were reduced, with no cracks detected by CT scanning in the samples prepared for RSE, which also showed lower porosity than earlier samples. By contrast, samples produced via tape casting showed poor adhesion, with repeated attempts to reproduce a usable tape unsuccessful due to adhesion issues with the casting substrate.

In conclusion, robocasting was confirmed to be a reliable and promising deposition technique for the GC2 glass-ceramic sealant, with the optimized paste formulation and printing parameters contributing to improved extrudability and joint quality. Nevertheless, residual porosity and crack formation remain open challenges that require further attention. Future work should focus on a more systematic characterization of the deposited paste through profilometer analysis, and the design of sample holders to assist in the weight placement step, repeated TGA testing of newly produced tapes, and continued refinement of the tape casting process as a potential complementary deposition route for the fabrication of OTM modules.

Contents

Abstract	ii
1 Introduction	1
1.1 Role of pure oxygen in energy transition	1
1.2 Uses of pure oxygen in industry	2
1.3 Technologies for pure oxygen production	4
1.4 Oxygen Transport Membranes	6
1.4.1 Working Principle	6
1.4.2 Materials used	8
1.4.3 Structure of OTMs	12
1.5 Modules with OTMs	13
1.5.1 Metal Supports	14
1.5.2 Glass-ceramic sealants	16
1.6 Additive Manufacturing: Robocasting	18
1.6.1 Ink formulation	19
1.7 Tape casting	20
1.8 Previous work and goal of thesis	21
2 Experimental Methods	24
2.1 GC2 Glass	24
2.1.1 Preparation of glass powder	26
2.1.2 Particle Size Analyzer	27
2.1.3 Differential Scanning Calorimetry (DSC) test	28
2.2 Preparation of glass paste for robocasting	29
2.2.1 Ink Formulation	29
2.2.2 Rheology Testing	31
2.2.3 Ink Deposition	33
2.2.4 Profilometer Analysis	36
2.3 Preparation of glass paste for tape casting	37

2.3.1	Ink Formulation	37
2.3.2	Tape casting process	37
2.3.3	Thermogravimetric Analysis (TGA)	39
2.4	Sample Preparation	40
2.4.1	Preparation of components for joining	40
2.4.2	Thermal Treatment Procedure	41
2.5	Sample Testing	44
2.5.1	X-Ray CT-Scan	44
2.5.2	SEM test	45
2.5.3	Leakage and Thermal Aging testing	47
3	Results and Discussion	48
3.1	GC2 Powder Test results	48
3.1.1	Particle Size Analyzer Test results	48
3.1.2	DSC Test results	49
3.2	Robocasting Paste Rheology	51
3.2.1	Flow Sweep Test results	51
3.2.2	3ITT results	55
3.3	Profilometer Test results	57
3.4	TGA of GC2 Tape	58
3.5	Tape formulation attempted changes	59
3.6	Sample Test results	61
3.6.1	CT Scan Test results	62
3.6.2	SEM Test results	70
4	Conclusion	76

List of Figures

1.1	Model representing the oxygen permeation steps through an asymmetric oxygen transport membranes [1]	8
1.2	Ideal perovskite structure [2]	9
1.3	Ruddlesden–Popper general crystal structure, with O_I belonging to the AO layer and O_{II} belonging to the perovskite layer [3]	10
1.4	Dual phase membranes of IC-EC and IC-MIEC type [3]	11
1.5	Fluorite structure of CeO_2 and CeO_2 doped with Pr^{3+} [4]	11
1.6	OTM configurations: a) Planar, b) Tubular, c) Hollow fiber [5]	13
1.7	3-end mode and 4-end mode, respectively [6]	14
1.8	An illustration of a planar OTM module in 4-end mode [7]	14
1.9	An illustration of a metal support: a) section view b) open view c) section view with feed and sweep gas streams during operation [8]	15
1.10	Different apparatus configuration for ink dispensing [9]	18
1.11	Representation of a tape caster [10].	21
2.1	Molten GC2 glass being poured on a metal plate at the end of the casting process	25
2.2	GC2 glass after cooling	25
2.3	Ball miller used	26
2.4	Sieve after usage	27
2.5	Mastersizer 3000+ from Malvern Panalytical	27
2.6	DSC 404 F3 Pegasus by Netzsch.	29
2.7	Rheometer used	31
2.8	Model on AutoCAD	34
2.9	Voxelizer printing parameters used for most samples	34
2.10	Voxelizer printing parameters used for samples produced for RSE	35
2.11	Robocasting process in progress.	35
2.12	Intra touch Ultra by Taylor Hobson	36
2.13	TQC Sheen tape caster and doctor blades (on top)	38

2.14	Metal samples with tape placed on them before joining process.	39
2.15	Machine used to perform TGA	39
2.16	Samples placed inside of Carbolite 1300 furnace with weights placed on top before thermal treatment process was initiated.	41
2.17	Carbolite 1300 furnace.	41
2.18	Thermal Treatment curve with a heating rate of $0.5^{\circ}\text{C}/\text{min}$ and a cooling rate of $0.5^{\circ}\text{C}/\text{min}$	42
2.19	Thermal Treatment curve with a heating rate of $0.5^{\circ}\text{C}/\text{min}$ and a cooling rate of $0.7^{\circ}\text{C}/\text{min}$	43
2.20	Thermal Treatment curve with a heating rate of $0.5^{\circ}\text{C}/\text{min}$ and a cooling rate of $0.8^{\circ}\text{C}/\text{min}$	44
2.21	CT-Scan in J-tech laboratory with 2 samples fitted in the sample holder	45
2.22	Sample prepared for SEM testing.	46
2.23	SEM JEOL JCM-6000Plus	47
3.1	Particle Size Analyzer test results for sieved GC2 batches 1 and 2 . . .	49
3.2	DSC test results for sieved GC2 batches 4 and 5	50
3.3	Flow sweep test results showing viscosity versus shear rate.	52
3.4	Different classifications of viscous fluids based on shear stress versus shear rate [31].	53
3.5	Flow sweep test results showing shear stress versus shear rate.	54
3.6	3ITT results for pastes, where the second interval simulates printing condition with print speed of 2mm/s. Shear rates are written at the top of each interval.	56
3.7	3ITT results for 80% solid load paste produced later during the thesis work, where the second interval simulates printing condition with print speed of 10mm/s. Shear rates are written at the top of each interval. .	57
3.8	Measured printed profile by profilometer. Resulting curve has been smoothened.	58
3.9	TGA and DTG curves superpositioned with zones of greatest mass changes highlighted	59
3.10	Tape during drying step	60
3.11	Top view of CT scanned LSCF - GC2 82.5% SL - Inconel 625, at glass-ceramic interface with membrane.	63
3.12	Top view of CT scanned 70CGO-30STF82 - GC2 82.5% SL - Crofer 22 APU, in the mid-section of the glass-ceramic layer.	64
3.13	Top view of CT scanned 70CGO-30STF82 - GC2 80% SL - pre-oxidized Crofer 22 APU, in the mid-section of the glass-ceramic layer.	65

3.14	Side view of CT scanned 70CGO-30STF82 - GC2 80% SL - pre-oxidized Crofer 22 APU. Side with a pore and poor adhesion of glass-ceramic to membrane is pointed at with an arrow	65
3.15	Top view of CT scanned 70CGO-30STF82 - GC2 80% SL - pre-oxidized Crofer 22 APU, in the mid-section of the glass-ceramic layer.	66
3.16	Top view of CT scanned RSE sample 1 (70CGO-30STF82 - GC2 80% SL - pre-oxidized Crofer 22 APU), at the glass-ceramic interface with membrane.	67
3.17	Closeup top view of CT scanned RSE sample 1, in the mid-section of the glass-ceramic layer. Some porosity can be seen. Furthermore, a crack is present (see red arrow).	67
3.18	Closeup side view of CT scanned RSE sample 1. Distances 1 and 3 are the width of the joint, and distances 2 and 4 are the thickness.	68
3.19	Top view of CT scanned RSE sample 2 (70CGO-30STF82 - GC2 80% SL - pre-oxidized Crofer 22 APU), in the mid-section of the glass-ceramic layer.	68
3.20	Closeup top view of CT scanned RSE sample 2, in the mid-section of the glass-ceramic layer. Some porosity can be seen, and no cracks were detected.	68
3.21	Closeup side view of CT scanned RSE sample 2. Distances 1 and 5 are the width of the joint, and distances 2 and 4 are the thickness.	69
3.22	Top view of CT scanned RSE sample 3 (70CGO-30STF82 - GC2 80% SL - pre-oxidized Crofer 22 APU), at the glass-ceramic interface with the metal.	69
3.23	Closeup top view of CT scanned RSE sample 3, in the mid-section of the glass-ceramic layer. Some porosity can be seen, and minor cracks were detected (not marked).	69
3.24	Closeup side view of CT scanned RSE sample 3. Distances 1 and 3 are the width of the joint, and distances 2 and 4 are the thickness.	70
3.25	SEM images of one side of the joint in the sample LSCF - GC2 82.5% SL - Inconel 625, with a closeup view on the right. Width of this side of the joint was measured to be around 2mm, and thickness around 206 μm	71
3.26	SEM image of one side of the joint in the sample LSCF - GC2 82.5% SL - Inconel 625 (2nd attempt). Width of this side of the joint was measured to be around 1.55mm, and thickness around 134 μm , noting that this side was overloaded during the joining process.	71

3.27 SEM images of one side of the joint in the sample 70CGO-30STF82 - GC2 82.5% SL - Crofer 22 APU, with a closeup view on the right. Width of this side of the joint was measured to be around 1.56mm, and thickness around 144 μm . Note the dense side (see red arrow) of the membrane.	73
3.28 SEM images of one side of the joint in the sample 70CGO-30STF82 - GC2 80% SL - pre-oxidized Crofer 22 APU, with a closeup view on the right. Width of this side of the joint was measured to be around 2.32mm, and thickness around 183 μm . Note the dense side (see red arrow) of the membrane.	74
3.29 SEM images of one side of the joint in the sample 70CGO-30STF82 - GC2 80% SL - pre-oxidized Crofer 22 APU, with a closeup view on the left. Width of this side of the joint was measured to be around 3.3mm, and thickness around 232 μm	74
3.30 Cross-sectional view by SEM of LSCF-V3 tape-Inconel 625 sample. Thickness of the glass-ceramic layer is noted to be 183 μm	75

List of Tables

1.1	Comparison of oxygen production technologies in terms of oxygen purity and typical energy use. Data adapted from Kiebach et al., 2022 [11]. . .	5
1.2	Inconel 625 chemical composition [12].	15
1.3	Crofer 22 APU chemical composition [13]	15
2.1	Composition of precursors used for GC2 glass formulation.	24
2.2	Composition of GC2 glass.	25
2.3	General formulation for the robocasting paste prepared	30
2.4	Procedure used for the preparation of robocasting paste	31
2.5	General formulation for the tape casting paste produced	37
2.6	Procedure used for the preparation of robocasting paste	38

1 Introduction

1.1 Role of pure oxygen in energy transition

As the global population grows, and as economies continue to expand, energy demand rises, placing enormous pressure on existing energy systems. Unfortunately, much of this demand is still met through fossil fuels, meaning that higher consumption brings higher emissions. Today, the energy sector accounts for about three-quarters of global greenhouse gas emissions, making it the largest contributor to climate change [14]. Meeting future energy needs without worsening environmental impacts requires a shift toward renewable alternatives and cleaner technologies that can support the transition away from conventional combustion. This growing urgency underpins international efforts to redesign the world's energy system and reduce emissions at their source.

The Paris Agreement commits the world to limiting global warming to well below 2°C while striving for 1.5°C, a target that requires rapid emissions reduction and deep structural changes across the energy system [15]. In support of this, the International Renewable Energy Agency (IRENA) envisions a global energy system in which renewables supply almost 90 percent of electricity by 2050, backed by efficiency gains, hydrogen production, and widespread carbon management technologies [16]. Within this transition, pure oxygen plays a surprisingly important role. One example is oxy-fuel combustion, where fuels are burned using pure oxygen instead of normal air. This approach raises combustion efficiency and produces exhaust that is mainly water vapor and CO₂, making carbon capture far more practical for power generation and industrial heat [17]. Pure oxygen is also tightly linked to the rise of green hydrogen: when hydrogen is produced through water electrolysis using renewable energy, the process generates oxygen as a high-purity co-product that can be reused in industrial systems rather than being wasted, supporting circularity and efficiency in clean energy supply chains [18]. Heavy industries such as steel are already using oxygen-enriched combustion to reduce fuel needs and lower emissions of CO₂ and nitrogen oxides, delivering cleaner production without rebuilding entire plants [19]. Pure oxygen also supports the

development of solid oxide fuel cells (SOFCs), which operate at high temperatures and can use oxygen to improve conversion efficiency, reduce impurities, and support low-carbon distributed power generation [20]. In addition, oxygen is crucial in biomass and coal gasification, where oxygen-fed reactors produce cleaner synthesis gas with higher energy content and enable easier CO₂ capture, making gasification both more efficient and compatible with future hydrogen systems [21]. Together, these applications show that pure oxygen, though not an energy source itself, improves efficiency, reduces pollution, and strengthens key technologies like carbon capture and green hydrogen, all which directly supports the pathways laid out by IRENA and the Paris Agreement for a climate-safe future.

Today, global pure oxygen production is substantial, with more than 85 million tons produced annually, driven primarily by industrial demand in steelmaking, chemicals, healthcare, and refining [22]. This demand is expected to increase as more sectors adopt carbon-capture systems, hydrogen technologies, and oxygen-based combustion to lower emissions, positioning oxygen supply as an increasingly important factor in the clean energy transition [22].

1.2 Uses of pure oxygen in industry

Pure oxygen plays a central role in industrial combustion processes, particularly where high temperatures and precise flame control are required. By replacing air with pure oxygen or oxygen-enriched mixtures, combustion systems avoid heating large volumes of inert nitrogen, resulting in higher thermal efficiency and lower fuel consumption. These improvements directly reduce carbon dioxide emissions per unit of output and significantly limit the formation of nitrogen oxides [19]. A prominent example is oxy-fuel combustion, where fuel is burned in oxygen and recycled flue gas, producing an exhaust stream mainly composed of CO₂ and water vapor. This configuration is especially attractive for industrial decarbonization because it simplifies carbon capture and supports integration with carbon capture and storage systems [17].

Building on advanced combustion, pure oxygen is also essential in gasification processes, where solid or liquid feedstocks are converted into synthesis gas. Using oxygen instead of air avoids nitrogen dilution, producing a cleaner syngas with higher energy content that is better suited for downstream conversion into power, hydrogen, or chemicals [21]. Oxygen-blown gasification improves process control and efficiency while reducing the volume of gas that must be treated. These characteristics make it a key enabling technology for low-carbon energy systems that combine fuel conversion with emissions control [21]. Coal gasification represents a specific and widely deployed ap-

plication of oxygen-based gasification. In this process, pure oxygen is used to partially oxidize coal at high temperatures, producing synthesis gas with minimal nitrogen dilution. Compared with air-blown systems, oxygen-blown coal gasification yields a higher energy content and makes CO₂ separation and capture more feasible for downstream conversion or storage, which supports low-carbon energy pathways [23].

Pure oxygen is also a critical input in gas-to-liquid (GTL) systems, where natural gas or synthesis gas is converted into liquid fuels and valuable chemicals. In GTL plants, oxygen is used in partial oxidation and reforming stages to produce synthesis gas (a mixture of hydrogen and carbon monoxide) with controlled composition. Using oxygen rather than air reduces nitrogen dilution in the feed, yielding a cleaner syngas that improves conversion efficiency, reduces the need for extensive syngas cleanup, and can lower by-product formation. These advantages also support better integration with carbon capture processes by producing a syngas stream that is easier to process in later stages [24].

In the glass industry, pure oxygen is widely used to enhance furnace performance while reducing environmental impacts. Oxygen-fuel combustion enables glass furnaces to operate at higher and more uniform temperatures, improving heat transfer and allowing the same production output to be achieved with lower fuel consumption. This leads not only to energy savings but also to improved glass quality and more stable furnace operation. At the same time, removing nitrogen from the combustion process significantly reduces NO_x emissions and lowers the volume of exhaust gases, which simplifies flue-gas treatment and contributes to a cleaner production overall [25].

Finally, pure oxygen plays a central role in metals oxidation processes, particularly in steelmaking and other metallurgical operations. In basic oxygen furnaces (BOFs), high-purity oxygen is injected into molten iron to oxidize carbon and other impurities, which accelerates the refining reactions and enables rapid, efficient steel production. The use of oxygen not only improves reaction kinetics but also reduces the need for external fuel, lowering overall energy consumption per ton of steel produced. Oxygen enrichment similarly benefits non-ferrous metallurgy by enhancing oxidation reactions, increasing throughput, and improving process efficiency in the production of metals such as copper and zinc. Given that metal production remains among the most energy-intensive industrial activities, the application of pure oxygen is a key factor in improving energy efficiency and lowering emissions across the metals sector [19].

1.3 Technologies for pure oxygen production

As the role of pure oxygen expands across combustion, gasification, metals processing, and low-carbon energy systems, the technologies used to produce oxygen become increasingly important. Oxygen production is itself energy intensive, and its cost, efficiency, and carbon footprint directly influence the feasibility of oxygen-based decarbonization pathways. Several mature and emerging technologies are currently used to separate oxygen from air or to generate it as a co-product, each suited to different scales, purity requirements, and industrial contexts.

Cryogenic air separation remains the dominant technology for large-scale, high-purity oxygen production worldwide. The process involves cooling air to extremely low temperatures so that its main components (oxygen, nitrogen, and argon) can be separated through fractional distillation. Cryogenic air separation units can deliver oxygen at purities exceeding 99 percent and at very high flow rates, making them essential for steelmaking, large oxy-fuel combustion systems, chemical production, and gasification plants. Their technical maturity and long operating lifetimes have made them the backbone of industrial oxygen supply for decades. However, cryogenic systems require substantial electricity input for air compression and refrigeration, meaning their environmental performance depends strongly on the carbon intensity of the electricity used [26].

Pressure swing adsorption provides a flexible and energy-efficient alternative to cryogenic air separation for small- to medium-scale oxygen production. In PSA systems, adsorbent materials are used to preferentially adsorb nitrogen from compressed air, allowing an oxygen-rich stream to be produced at purities typically in the 93–95 percent range. These systems feature relatively simple equipment design, modularity, and ease of operation, making them well suited for applications such as decentralized industrial sites, wastewater treatment, and medical oxygen supply. Compared with cryogenic units, PSA units generally require less energy at smaller scales and have lower capital costs, though they become less competitive as demand grows or when ultra-high oxygen purity is required. [27].

Electrolysis represents a fundamentally different pathway for oxygen production, as pure oxygen is generated as a co-product during the production of hydrogen from water. In electrolyzers, electricity splits water molecules into hydrogen and oxygen, producing very high-purity oxygen without the need for conventional air separation. As the green hydrogen economy expands, the volume of oxygen produced alongside hydrogen is also expected to grow substantially, and this oxygen can be captured and utilized in nearby industrial processes such as oxy-fuel combustion, gasification, or wastewater

treatment. By integrating oxygen utilization with hydrogen systems, overall efficiency can be improved and the need for dedicated oxygen production infrastructure reduced, particularly in industrial clusters where both hydrogen and oxygen demand coexist [18].

Alongside established oxygen production technologies, oxygen transport membranes (OTMs) are emerging as a promising option for future oxygen supply, particularly for applications requiring high-purity oxygen closely integrated with high-temperature industrial processes. OTMs are typically dense ceramic membranes that separate oxygen from air at elevated temperatures using mixed ionic–electronic conducting materials. Compared with cryogenic air separation and PSA systems, OTMs can continuously produce very pure oxygen (>99 percent), and their design allows thermal integration directly with processes such as oxy-fuel combustion, gasification, or catalytic reactors, which can significantly reduce the additional energy required for oxygen separation. The modular nature of OTM reactors and their potential for lower capital and operating energy demand make them attractive for both decentralized and medium-scale industrial applications. While challenges remain for commercial deployment at very large scales, ongoing research and pilot activities indicate that OTMs could play an important complementary role in clean industrial oxygen supply and decarbonization pathways [11].

Taken together, these technologies define a diverse oxygen production landscape that mirrors the wide range of industrial applications discussed in the previous section. Cryogenic air separation continues to underpin large, centralized oxygen supply; pressure swing adsorption enables flexible and decentralized production for smaller-scale users; and water electrolysis directly links oxygen generation to the rapid expansion of renewable hydrogen systems. Within this landscape, oxygen transport membranes stand out as a promising next-generation option, offering the potential for closer integration between oxygen supply and high-temperature industrial processes.

Technology	Oxygen Purity	Typical Energy Use (kWh/tonne O ₂)
Cryogenic Air Separation	~99%	220–245
Pressure Swing Adsorption (PSA)	~95%	245–525
Electrolysis	>99.5%	~1320
Oxygen Transport Membranes (OTMs)	>99%	147–185

Table 1.1: Comparison of oxygen production technologies in terms of oxygen purity and typical energy use. Data adapted from Kiebach et al., 2022 [11].

1.4 Oxygen Transport Membranes

1.4.1 Working Principle

Oxygen Transport Membranes (OTMs) are gas-tight ceramics made from mixed ionic and electronic conductors (MIEC) that allow oxygen to permeate selectively from a feed to a permeate side. The transport mechanism in OTMs involves the simultaneous movement of oxygen ions and electrons through the solid lattice, driven by the difference in oxygen partial pressures across the membrane, with the diffusion process being thermally activated at high temperatures (typically above 500°C) [11]. At the feed side, molecular oxygen adsorbs onto the membrane surface, dissociates into oxygen atoms, and is reduced by electrons from the membrane bulk to form oxygen ions (1.1):



The operation of these membranes relies on the presence of oxygen vacancies within the crystal lattice, typically associated with perovskite-type ($\text{ABO}_{3-\delta}$) or fluorite-type structures. Once the oxygen ions are incorporated into the lattice at the feed side (high $p\text{O}_2$), they migrate through these vacancies toward the permeate side (low $p\text{O}_2$). To maintain local electroneutrality during this ionic flux, a compensatory flow of electrons or electronic holes occurs in the opposite direction. At the permeate interface, the reverse reaction (1.2) takes place, where the oxygen ions are oxidized, releasing electrons back into the ceramic bulk and recombining to form molecular oxygen gas:



The driving force for this continuous transport is the chemical potential gradient established by the oxygen partial pressure ratio ($p\text{O}_{2,\text{feed}}/p\text{O}_{2,\text{perm}}$). In the steady state, the total oxygen flux (j_{O_2}) can be modeled by the Wagner equation (1.3), which integrates the partial conductivities of the species involved [11]. Assuming that the membrane is sufficiently thick such that bulk diffusion dominates over surface exchange kinetics, the oxygen permeation flux can be expressed as:

$$j_{\text{O}_2} = \frac{RT}{16F^2L} \int_{p\text{O}_{2,\text{perm}}}^{p\text{O}_{2,\text{feed}}} \frac{\sigma_{\text{ion}}\sigma_{\text{el}}}{\sigma_{\text{ion}} + \sigma_{\text{el}}} d \ln p\text{O}_2 \quad (1.3)$$

where R is the gas constant, T is the absolute temperature, F is the Faraday constant, L is the membrane thickness, σ_{ion} and σ_{el} are the ionic and electronic conductivities respectively, and $p\text{O}_{2,\text{feed}}$ and $p\text{O}_{2,\text{perm}}$ are the oxygen partial pressures at the feed and

permeate sides respectively. For many high-performing MIEC materials, the electronic conductivity is significantly higher than the ionic conductivity ($\sigma_{el} \gg \sigma_{ion}$), meaning the total transport is primarily limited by the rate at which oxygen ions can hop through the oxygen vacancies in the lattice.

A critical aspect of OTM performance is identifying which part of this multi-step process limits the overall permeation rate, which is referred to as the rate-determining step (RDS). This is not a fixed property but varies depending on operating conditions and membrane geometry, such as temperature and membrane thickness. To help determine the RDS in oxygen transport, Bouwmeester et al. defined the characteristic thickness, L_c (1.4) [3]. It is mathematically defined by the ratio of the oxygen self-diffusion coefficient (D_s) to the surface exchange coefficient (k_s) [11]:

$$L_c = \frac{D_s}{k_s} \quad (1.4)$$

This parameter represents the threshold where the resistance from bulk diffusion equals the resistance from surface exchange. If the physical thickness of the membrane L is much greater than L_c , bulk diffusion acts as the RDS, while when L is much smaller than L_c , the surface exchange kinetics become the RDS [11]. Therefore, decreasing the thickness of membranes can increase oxygen permeability for membrane materials controlled by bulk diffusion. However, for membrane materials controlled by surface exchange, this reduction in thickness would not affect oxygen transport. Instead, improvements must come from enhancing the surface catalytic activity, for instance, by applying a porous activation layer or increasing the surface area [3]. A good balance of properties can be reached through the usage of asymmetric membranes made of a thin selective membrane layer (10 – 30 μm) supported on a relatively thick porous support (200 – 500 μm) [1].

The oxygen permeation process through asymmetric membranes can be described by six different steps. A model showing these steps as a series of resistances is shown in Figure 1.1. Zones I and VI describes the concentration polarization effects in the gas phases on the feed and sweep sides of the membrane. Zone V refers to concentration polarization occurring within the pores of the porous support layer. Zone II represents the surface exchange processes on the high oxygen partial pressure side, including oxygen reduction, dissociation, and incorporation into the oxide lattice. In contrast, zone IV illustrates the reverse surface reactions on the low oxygen partial pressure side, where oxygen ions are converted back into molecular oxygen. Finally, zone III corresponds to the bulk transport of oxygen ions through the dense, selective membrane layer [1].

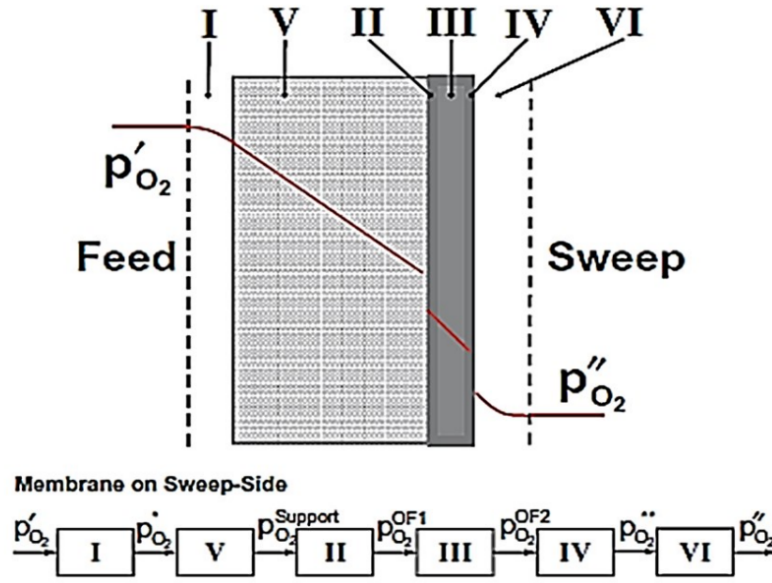


Figure 1.1: Model representing the oxygen permeation steps through an asymmetric oxygen transport membranes [1]

1.4.2 Materials used

The materials used for the manufacturing of OTMs should meet certain criteria in order to maintain the performance of the oxygen permeation process under the working conditions. A high mixed ionic-electronic conductivity is central for the operation of OTMs, therefore a suitable MIEC material should be selected. An OTM device typically works under high temperatures (in the range of ~ 800 - 1000°C), and should be able to resist such harsh working conditions for more than 40,000 hours at least without any noticeable degradation in its efficiency. Other qualities include low polarization resistance, a high oxygen flux ($\geq 10^{-6} \text{ mol s}^{-1} \text{ cm}^{-2}$), a thermal expansion coefficient that is similar to the materials it is joined to, a high mechanical strength, and excellent thermal cycling resistance. [2]

For OTMs, there are two main types based on the number of phases in the membrane's composition: single-phase and dual-phase.

(1) Single-phase OTMs

Single-phase membranes consists of one type of material that is conductive of both ions and electrons (MIEC). This type of OTM has been well-studied for some decades now, with most single-phase OTMs having either a perovskite or Ruddlesden–Popper crystal structure [11].

Perovskite materials have the general formula ABO_3 , which commonly corresponds to $A^{2+}B^{4+}O_3$ (although $A^{1+}B^{5+}O_3$ or $A^{3+}B^{3+}O_3$ are also possible), with A and B being two cations of different sizes such that A-atoms are larger than B-atoms [11]. The A-atom is usually a divalent or trivalent rare earth or alkaline earth element ion such as La or Sr, and the B-atom is typically a trivalent or tetravalent transition metal ion such as Fe, Co or Nb [3]. In Figure 1.2, the ideal perovskite structure can be seen. When the A or B-site in a standard perovskite is replaced or partially substituted by other metal ions, it leads to a formation of anion defects or B-site ions with different valences. Such materials are referred to as complex oxides and are characterized by high oxygen permeability and excellent overall performance [3].

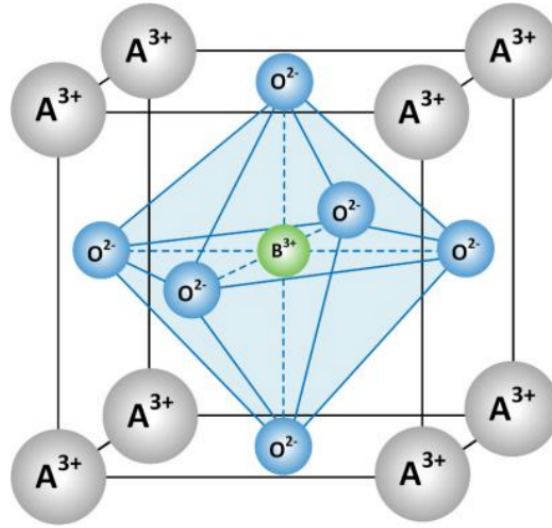


Figure 1.2: Ideal perovskite structure [2]

From the various combinations of chemical compounds, the ones with the highest oxygen permeability are $Ba_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (BSCF) and $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF). In the case of BSCF, despite its good performance, it has some disadvantages that limit its usage as a membrane material, namely its instability in atmospheres rich in CO_2 or SO_2 , and its high chemical and thermal expansion. In the 850-900°C range, which is typically in the working temperature range of OTMs, lattice expansion from a cubic to a hexagonal structure may lead to chemical instability and mechanical failure. LSCF has been extensively investigated as a membrane material and also as a cathode material for Solid Oxide Fuel Cells (SOFCs). It is characterized with a high electronic conductivity and good ionic conductivity. A drawback though is that LSCF is unstable in SO_x -containing atmospheres due to the formation of $SrSO_4$. This limitation makes LSCF unsuitable for OTM applications that require stability under low oxygen partial

pressure conditions or in environments containing SO_x species, although studies have shown that LSCF is quite stable in CO_2 if the Sr-content is low.[11]

Ruddlesden–Popper materials can be described with the general notation $A_{n+1}M_nO_{3n+1}$ (with $n = 1, 2, 3, \dots \infty$). In this notation, A is a cation with a large radius, such as lanthanide and alkaline earth elements, and M is a transition metal, such as Cu, Ni, Co [11]. Its structure is made of a series that alternate between perovskite layers and rock-salt (AO) layers, with a representation of the structure seen in Figure 1.3 [3].

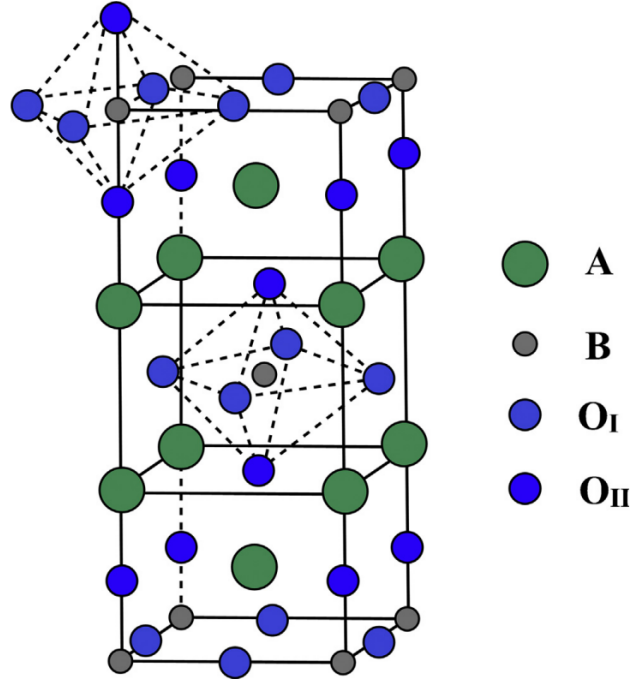


Figure 1.3: Ruddlesden–Popper general crystal structure, with O_I belonging to the AO layer and O_{II} belonging to the perovskite layer [3]

An example of such materials is $\text{Ln}_2\text{NiO}_{4+\delta}$ (with $\text{Ln} = \text{La, Pr, Nd}$, and other rare earth metals). They are characterized with good ionic and electronic conductivity, and in comparison to perovskite OTM materials, have higher oxygen diffusion and better thermal expansion performance. A notable drawback is its relatively low oxygen permeability, therefore further research is required to improve its oxygen permeability [3].

(2) Dual-phase OTMs

Dual-phase membranes are composed of both a stable ionic conductor and a stable electronic conductor, with this stability presenting an advantage over single-phase membranes. Ideally, the presence of two phases combines the characteristics of both compounds that are used to achieve, in the working conditions of a typical OTM, a

large oxygen permeability and good mechanical and chemical stability [11]. For dual-phase membranes, they can be a combination of an ionic conductor (IC) and either an electronic conductor (EC) or a mixed conductor (MIEC), with a representation present in Figure 1.4. [3]

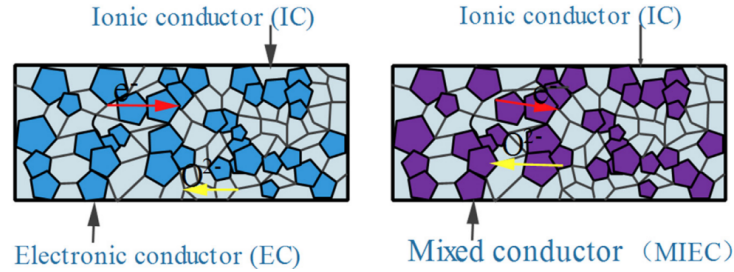


Figure 1.4: Dual phase membranes of IC-EC and IC-MIEC type [3]

In the case of IC-EC dual phase membranes, the most commonly used material for the IC phase are fluorite-type oxides. These oxides have a general formula of AO_2 , with A being a large tetravalent cation such as Zr^{4+} and Ce^{4+} [11]. Some examples of such oxides include Yttria-stabilized zirconia (YSZ), Bi_2O_3 , and CeO_2 (see Figure 1.5). In particular, CeO_2 has some advantages related to its high ionic conductivity, lower working temperatures (with respect to YSZ), and robust stability (compared to Bi_2O_3). A disadvantage of this material is that it can easily be reduced (from Ce^{4+} to Ce^{3+}) in working conditions with a reducing atmosphere, which could lead to negative side effects such as undesired chemical expansion, which is unsuitable in the case of SOFC applications. One solution to reduce such phenomena is to dope CeO_2 with lanthanide elements with low or fixed valence states such as Tb or Pr, leading to an increase in oxygen vacancies (see Figure 1.5). As a result, the mobility of oxygen ions is improved. For the EC phase, noble metals such as Au, Ag, Pd, and Pt used to be

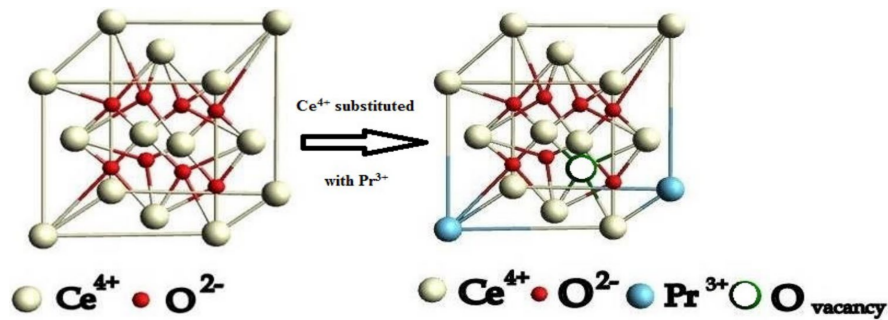


Figure 1.5: Fluorite structure of CeO_2 and CeO_2 doped with Pr^{3+} [4]

used, but it was found that only when the volume ratio of the noble metals in the membrane is 30-40% can the electronic conductivity path be continuous. Moreover,

there were issues related to thermal expansion coefficient mismatch, and the fact that it was expensive to produce such membranes due to the high costs of the metals. As an alternative to noble metals, some perovskite or spinel oxides can be used, such as $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}\text{-La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (perovskite) or MnFe_2O_4 (spinel oxide) [3].

For IC-MIEC dual phase membranes, instead of having a pure EC phase, MIEC oxides such as $\text{Ln}_x\text{Sr}_{1-x}\text{FeO}_{3-\delta}$ (Ln = rare earth metals) are used. The main goal of replacing an EC phase with a MIEC one, is to improve the blocking effect of oxygen ions, which can be present in IC-EC dual phase membranes due to the IC phase inhibiting the oxide ions transport. In Figure 1.4 the motion of the oxygen ions for both types of dual-phase membranes can be noted by the yellow arrows [3].

For this thesis both single and dual-phase OTMs were employed, with samples of LSCF single-phase membranes and samples of 70CGO-30STF82 dual-phase asymmetric membranes used, with a CTE of $13.8 \times 10^{-6} \text{ K}^{-1}$ and $12.5 \times 10^{-6} \text{ K}^{-1}$ respectively. The dual-phase membrane consisted of CGO ($\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$) as the IC phase and STF82 ($\text{SrTi}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$) as the MIEC phase [28].

1.4.3 Structure of OTMs

OTMs are most commonly fabricated in three different geometries: planar, tubular, and hollow fiber configurations (see Figure 1.6). Out of the three configuration, the planar is the cheapest and easiest to manufacture, making them the most commonly used out of the three geometries. A drawback of planar OTMs is that their performances are limited by the low surface area and high-temperature sealing. In the case of tubular OTMs, they have a large exchange area, allowing them to achieve better performance than the planar configuration. An added benefit of this configuration is that pressure drops are considerably lower than those found in planar OTMs. Hollow fiber configurations possess the large surface area out of the three geometries, and are characterized with their thin walls (much thinner than the planar and tubular membranes), allowing them to achieve the best performance out of the three configurations. The main issue associated with this type of membrane lies in the challenge to achieve reliable sealing and scaling the technology up to industrially relevant sizes. [5, 11].

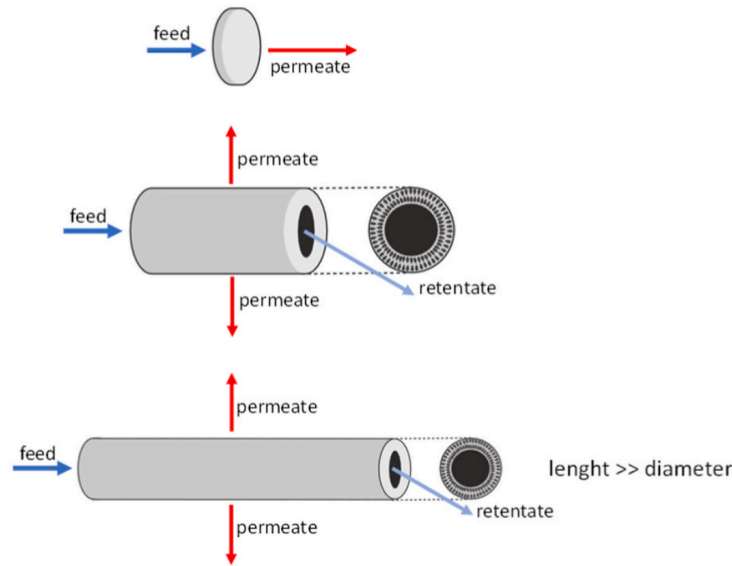


Figure 1.6: OTM configurations: a) Planar, b) Tubular, c) Hollow fiber [5]

For this thesis, the planar configuration was utilized.

1.5 Modules with OTMs

In order to use OTMs effectively in industrial processes, they must first be integrated into modules. OTM modules consist of multiple single repeating units (SRU) joined together in series or parallel configuration consisting of three layers each: the membrane, the metal support, and a glass-ceramic sealant material. There are two main configurations that are differentiated by their operation mode and membrane integration: 3-end mode and 4-end mode (see Figure 1.7) [8]. In the 3-end mode configuration, the driving force for oxygen transport, defined by the oxygen partial pressure gradient, is generated by applying a vacuum on the permeate side of the membrane. In contrast, the 4-end mode relies on a sweep gas flowing along the permeate side to establish the required driving force. Since membranes in the 4-end mode are directly integrated into the plant, flue gases are typically used as the sweep gas. Unlike this arrangement, membranes operating in the 3-end mode are indirectly integrated into the power plant, and no sweep gas is employed [6].

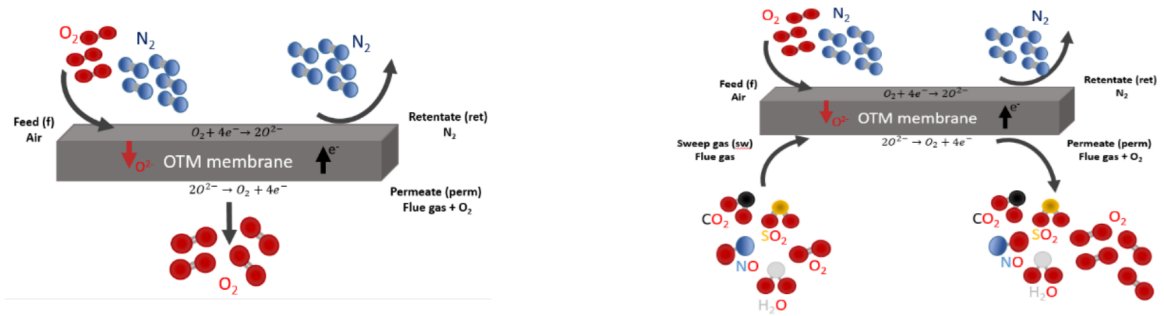


Figure 1.7: 3-end mode and 4-end mode, respectively [6]

An example of a complete OTM module is illustrated in Figure 1.8. There are many other ways that the OTM module can look like depending on its design parameters such as the geometry of the OTM, mode of operation, and the way that the SRUs were connected together.

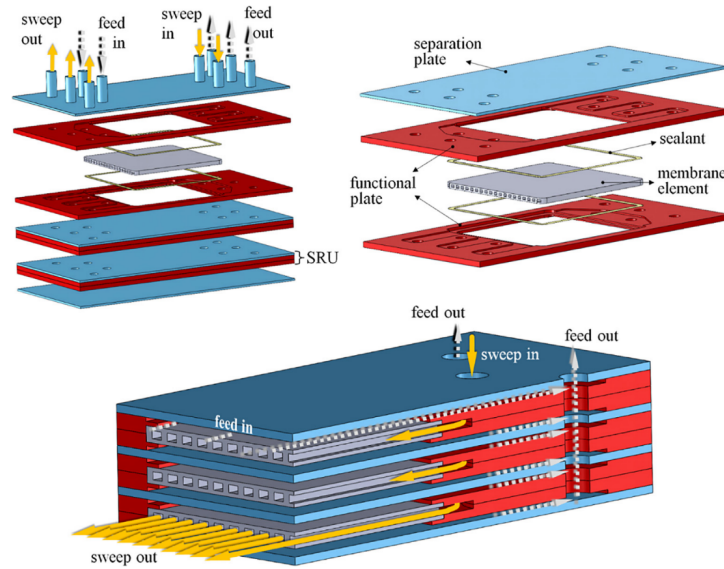


Figure 1.8: An illustration of a planar OTM module in 4-end mode [7]

1.5.1 Metal Supports

A critical aspect of OTM modules are the metal supports, which have a central role in the stability of the overall structure. They hold in place the SRU units and help in the equal distribution of heat in the module during the working process. The metal chosen should also have a coefficient of thermal expansion (CTE) that is compatible with both the membranes and glass-ceramic sealant to avoid the failure of the module during working conditions, and must also be resistant to high-temperature corrosion [8]. Metal supports should also be designed to accommodate distribution channels to

assist in the inlet and outlet flow of the gases to and from the module during operation, and must be compatible with external systems that are to be connected to the module during operation. An example of a metallic case can be seen in Figure 1.9.

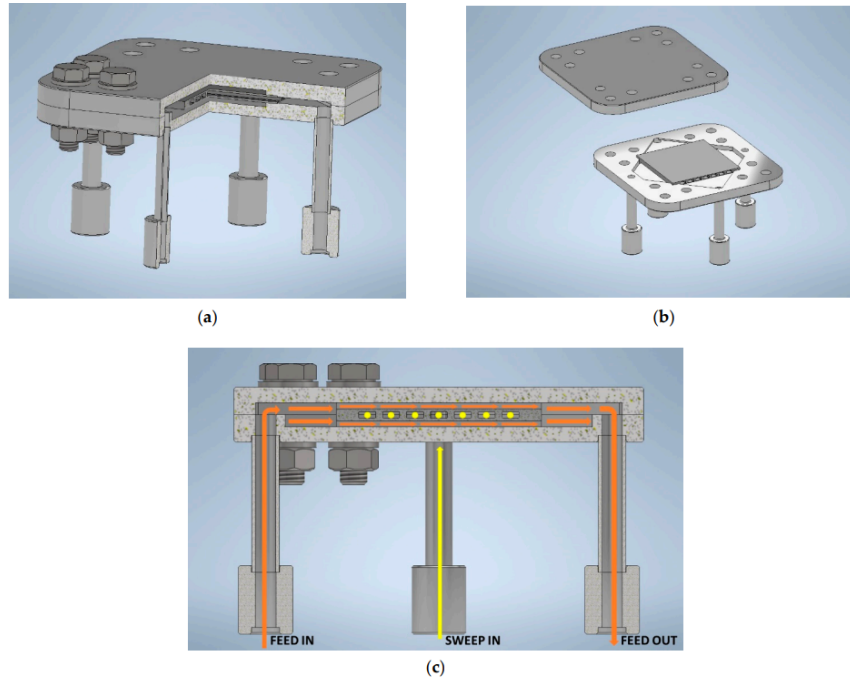


Figure 1.9: An illustration of a metal support: a) section view b) open view c) section view with feed and sweep gas streams during operation [8]

Given the harsh environment during the working operation, metal alloys such as Inconel 625 (see Table 1.2) or Crofer 22 APU (see Table 1.3) can be used.

Element	Cr	Mo	Nb	Fe	Al	Ti	C	Mn	Ni
%	20–23	8–10	3.15–4.15	≤ 5	≤ 0.4	≤ 0.4	≤ 0.1	≤ 0.5	Bal.

Table 1.2: Inconel 625 chemical composition [12].

	C	Cr	Fe	S	Mn	Si	Ti	Cu	P	Al	La
Min. %		20.0	Bal.		0.30		0.03				0.04
Max. %	0.03	24.0		0.020	0.80	0.50	0.20	0.50	0.050	0.50	0.2

Table 1.3: Crofer 22 APU chemical composition [13]

Inconel 625 is a nickel-based face-centered cubic (FCC) superalloy that had been strengthened via the solid-solution hardening effect of refractory metals such as niobium and molybdenum, which are present in the nickel-chromium matrix of the metal. This alloy is widely used in a wide range of industries and over a broad temperature range, such as in petrochemicals, aerospace, chemical and marine applications.

It facilitates an ideal combination of yield, fatigue and creep strengths, in addition to good resistance to oxidation, corrosion and frictional wear in harsh environments. Initially, Inconel 625 was designed to be a solid-solution strengthened material with a precipitated microstructure, which is valid in temperature ranges below and above the 650-875 °C temperature range, in which intermetallic and carbide precipitates form that play a critical role in the strength possessed by the alloys. Increasing the temperature above 875 °C could allow the intermetallic precipitate phases to dissolve completely into the crystal matrix, which explains the characteristic of this superalloy in replenishing its creep properties which leads to an increase in the material's lifetime [12]. In terms of the CTE, Inconel 625 has a CTE of $13.1 \times 10^{-6} \text{ K}^{-1}$ which is close to the CTE of LSCF ($13.8 \times 10^{-6} \text{ K}^{-1}$), with these values for CTE provided by Francesco da Prato.

Crofer 22 APU is a ferritic high-temperature stainless steel that has been mainly designed for high temperature applications such as in solid oxide fuel cells (SOFCs). They are characterized by excellent corrosion resistance, good workability and a low rate of chromium evaporation. At around 900 °C, a surface layer of chrome manganese oxide forms, which is characterized with high thermodynamic stability and good electrical conductivity. This layer is useful in the joining process, as it prevents chromium diffusion into the adjacent glass-ceramic layer, which can lead to failure during thermal aging. In terms of the CTE, it is characterized with a CTE of $11.5 \times 10^{-6} \text{ K}^{-1}$, which is quite compatible with the CTE of the dual-phase OTM which has a CTE of $12.5 \times 10^{-6} \text{ K}^{-1}$ [13, 29].

In the case of the metal support prepared by RSE, previously it was designed to be the one seen in Figure 1.9. This was later changed to a circular planar model with the ability to incorporate multiple membranes.

1.5.2 Glass-ceramic sealants

A critical section of an OTM module is the joint, or sealant, which is responsible with keeping the OTM connected to the metal support. The sealant should provide good gas tightness to avoid gas leakages, have long-term stability under working conditions, and have a CTE that is similar to both the OTM and metal support to avoid high thermal stresses from occurring which would lead to early failure [8].

Three different sealant material categories can be defined: compressive seals, compliant seals, and rigidly bonded seals. Compressive seals require a constant load and are deformable, therefore, no CTE match between the components of the module is required. However, applying a constant compressive load makes the system more complex and more prone to failure, which can lead to higher gas leakages than rigidly bonded seals. Compliant seals typically utilize deformable metals such as copper, sil-

ver and AG-Cu-Ti brazing. Similar to compressive seals, they undergo loads and are deformable. However, the harsh environments of the working conditions and interactions with the fuel and oxygen environments during operational usage can lead to corrosion and degradation [30].

Of the three sealant categories, rigidly bonded seals have the best gas tightness, and are the most widely employed in the energy production sector. They are typically glass-ceramic materials, and are bonded to the adjacent materials, therefore the selection of the appropriate glass-based material is crucial in order to avoid CTE mismatch. A benefit of using this sealant is that their properties can be tailored in terms of wettability, thermal expansion, and thermodynamic stability by choosing the correct material composition. Additionally, pressure-less deposition of glass can be done, making the joining process easier. For the selection of the appropriate glass-based sealant, the compatibility of the CTE between the sealant and the materials adjacent to it is of utmost importance. Minimizing CTE mismatch ensures that no cracks or fissures occur during operation, which would lead to the failure of the device. Another criteria that should be considered is the glass transition temperature (T_g) and the softening temperature (T_s), according to the working conditions of the device [8].

For choosing the appropriate glass, the composition of the glass should be carefully selected as it would greatly influence the properties of the sealant. The glass network consists of three main components: glass formers, modifiers, and intermediate oxides, where the later two components alter the glass network built by the glass formers. With the addition of both modifiers and intermediate oxides, the T_g and T_s of the glass would therefore change. T_g is defined as the temperature below which the glass acts as a rigid, brittle material, while above T_g the glass becomes flexible. At the T_s point, the glass becomes less viscous as it transforms into a plastic state. With T_s being a known parameter of the glass-ceramic material, the joining process is done by sintering in a high temperature furnace for a certain period of time at temperatures above T_s to ensure that the glass flows effectively in its low viscosity state. The flow of the glass-ceramic material would ensure effective wetting of the adjacent surfaces, providing good adhesion to the materials and high gas tightness [30].

Furthermore, glass is a non-equilibrium amorphous structure, which at certain temperatures can undergo crystallization. Through thermal treatment, the growth of crystallized phases in the glass structure results in the material becoming a glass-ceramic, which consists of mostly crystalline phases with residual glassy phases. The amount of crystallized phases that are present after thermal treatment changes depending on the composition of the glass, which affects the material's overall properties. Regarding the residual glass phases present, they are still amorphous and can soften at high

temperatures, therefore helping with the sealing. To ensure that the glassy phase does not soften too much, T_s should be higher than the working temperature.

In this thesis work the glass used was GC2, which is a type of borosilicate glass. Its preparation and composition is explained later in this report.

1.6 Additive Manufacturing: Robocasting

Three-dimensional printing is an emerging technology that allows the building of 3D parts by using computer-aided design (CAD) models by adding materials layer-by-layer, which is a reason to why it is also referred to as additive manufacturing. A benefit of this method is that unlike other conventional manufacturing methods is that it allows the creation of complex structures with high resolution and minimal material waste. Only required material is deposited during the printing process, therefore the waste material is minimized. Additive manufacturing has been used with different types of materials, such as polymers, metals and ceramics. In the case of ceramic inks, the most promising method is direct ink writing (DIW), which is also referred to as robocasting [31].

Robocasting, or DIW, uses the concept of material extrusion in order to deposit a flowable paste through a nozzle, with the pattern of ink deposition following a CAD model that had been previously designed and uploaded to the machine's software. The extrusion process is done by applying an external pressure that is controlled by the printing program. There are different apparatus configurations that can be used to apply the external pressure, as seen in Figure 1.10. For this thesis work, piston-driven dispensing was used [9, 31].

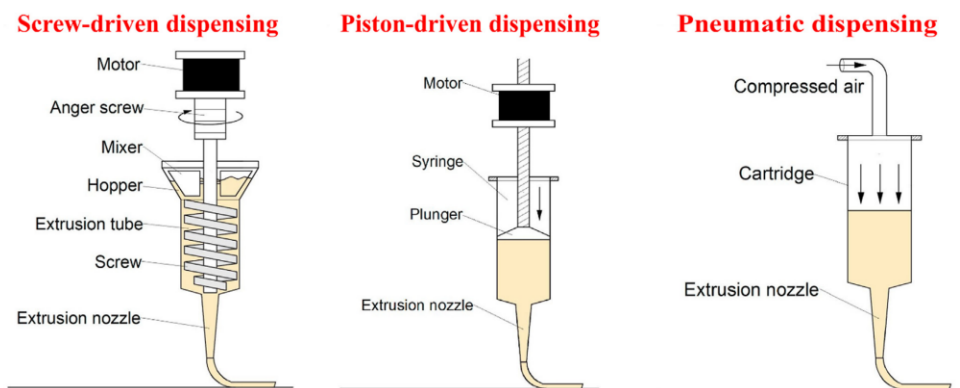


Figure 1.10: Different apparatus configuration for ink dispensing [9]

Robocasting offers multiple advantages when compared to other conventional methods. It offers the ability to quickly fabricate complex structures at an affordable cost

and can be used with multiple types of materials with minimal material waste. Therefore, robocasting can be considered to be an eco-friendly technique. DIW is also typically done in air at ambient environment condition, making it easier to set up than many conventional techniques [9].

For the deposition of the glass sealant, robocasting was mainly used in this thesis work.

1.6.1 Ink formulation

Ceramic inks for robocasting consist of highly concentrated suspensions of ceramic particles, which are also known as ceramic pastes or slurries. The ink's formulation is the most critical step in robocasting, as it must be homogeneous, should have a high solid load to minimize shrinkage, and must meet the required rheological properties to achieve good shape fidelity and structural stability post-printing. Regarding the paste's rheological properties, the ink must be smoothly extruded through a nozzle without any clogging or gaps, leading to the formation of continuous filaments. Furthermore, after extrusion, the filaments should be able to retain the shape of the nozzle, accurately reproduce the programmed printing path, and have the ability to support layer stacking. In short, the paste should be extrudable, have shape-retention capacity and be self-supporting [31].

To meet the rheological requirements, ideally the DIW paste should behave like a fluid during extrusion, and exhibit an elastic behavior once it is at rest after the extrusion process is completed. Two main approaches have been done to achieve ceramic pasties with these properties, colloidal suspensions and gel-embedded suspensions. Colloidal suspensions are highly concentrated slurries of ceramic particles with around 60-80 wt% solid load in a low viscosity liquid, with a small amount of organic additives that assists in adjusting the interparticle forces. By tuning the solid loading and tailoring the interparticle interactions in the ceramic paste's medium, it is possible to achieve an adequate extrusion process while ensuring that the paste has good structural integrity. Extrudability can be further enhanced by the addition of a dispersant or plasticizer in the slurry, where they are typically based on cellulose-based polymers. A disadvantage of colloidal suspensions is that they are very sensitive to variations on the chemistry and pH of the environment, making them typically difficult to control. An alternative to colloidal suspensions that have been recently developed are gel-embedded suspensions. The main difference between them is that the rheological properties of gel-embedded suspensions are not directly derived from interparticle interactions, but from the properties of the gel phase where the ceramic particles are dispersed in. As a result, the suspensions are more stable when compared to colloidal

suspensions, but at the expense of the solid load, which is reduced. Hydrogels, such as those based on cellulose, are typically used due to their ease at being manipulated and due to the low volatility of water when compared to other solvents. Organogels, which are based on a polymer dissolved in an organic solvent, can also be used, although they are less common. Most gel-embedded suspensions depend on the liquid to solid transition via solvent evaporation just after filament deposition. Gel-embedded suspensions has the advantage of being potentially compatible with any ceramic powder, since their behavior is not based on the surface chemistry of the particles [31].

DIW pastes can be classified as pseudoplastic or shear-thinning materials, because their viscosity decreases as the shear rate increases, with the viscosity higher at rest conditions, such as in the nozzle before extrusion or on a sample after printing is completed. This behavior is caused due to the disruption of the interactions within the paste or due to the ordering of the particles or molecules in the direction of flow from an initial rest state. The lower viscosity is important to ensure that the paste flows more easily while requiring lower applied pressure. Furthermore, the printed paste filament should show a thixotropic behavior, where after extrusion is completed, the paste should quickly regain a higher viscosity in order to maintain the nozzle shape and maintain structural stability [31].

In this thesis work, a colloidal suspension was utilized in the ink formulation process.

1.7 Tape casting

Another method that can be used to fabricate the sealant layer is tape casting. Tape casting is a well established industrial process that offers many advantages. It does not need complex infrastructure, is scalable, can be performed continuously, and is cost-effective. Furthermore, it offers high flexibility in controlling the thickness and properties of the fabricated films [32].

In tape casting, a slurry is spread over a flat surface via carefully controlled blades that are referred to as doctor blades. As a result, very thin films, as thin as $1\ \mu\text{m}$, can be prepared. The parameters influencing tape casting are mainly related to the material contents of the slurry, such as the powder, solvent and additives, and also the device configuration, such as the doctor blade height and velocity of spreading. Therefore, careful control of such parameters are required to have an effect tape casting process [33].

Tape casting thin films of glass or ceramic pastes involves a series of steps. First the slurry has to be prepared by mixing the intended powder, such as ceramic or glass powders, in a solvent with additives such as dispersants and binders in order to ensure

that the slurry has good homogeneity and that the resulting tape has good mechanical properties such as flexibility, and good density post thermal treatment processes [33]. Its viscosity should be lower than that of the slurry prepared for robocasting in order to ensure the ease of spreadability of the slurry during the tape casting process. Using a tape caster, which are devices used to assist in the automation of the process, the slurry can then be poured between the gaps of the doctor blades. Following this, the blades movement can be controlled through the program of the tape caster by setting the speed. For the thickness of the film, the doctor blades can be fine tuned to achieve the desired thickness before the slurry spreading process can be started. Typically, the slurries are spread over silicon-coated mylar, a type of polyester film, as it allows an easier removal of the film after drying. Drying is the final step, with the time and method used mainly depending on the solvent used to make the slurry. After drying, the film can be removed and shaped in way that is desired before being used for its required application. An example representation of a tape caster is shown in Figure 1.11.

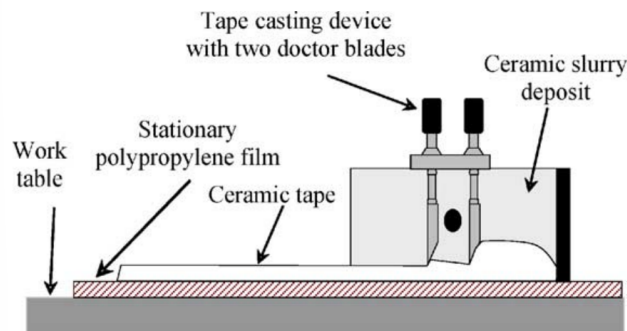


Figure 1.11: Representation of a tape caster [10].

In the case of this thesis work, tape casting was attempted to produce a film to use as a glass sealant.

1.8 Previous work and goal of thesis

Politecnico di Torino's Department of Applied Science and Technology (DISAT), which specializes in research into the materials and their engineering applications including for energy purposes, was where the thesis work was done. Ricerca sul Sistema Energetico, RSE S.p.A., a company based in Milan that focuses in the analysis, study and research related to the energy sector, had been conducting research on OTMs. This research involves the development of ceramic membranes along with its integration in industrial processes in order to study their energy and economic advantages.

Furthermore, the research focuses on the modeling and design of the membrane module. Designing a membrane module that is suited for industrial integration requires a solution to the issue of joining a ceramic membrane to a metal, which a module is typically made of. A joint must be able to withstand high working temperatures and pressure conditions, while at the same time providing effective sealing and have a compatible CTE with the adjacent materials. Chemical stability is also required in order to avoid any reactions with the materials in contact and working environment. RSE had been working in collaboration with DISAT to find a solution for this issue, with focus on the identification and improvement of a suitable joint. RSE throughout the thesis work provided the OTMs and metal supports for testing. DISAT, furthermore, specializes in the preparation of glass or glass-ceramic materials and their characterization in order to create joints given the application. Based on the details provided by RSE on the characteristics of the membranes, DISAT was able to identify a suitable glass, GC2, that is suitable for the fabrication of a glass-ceramic sealant, due to it showing promising sealing properties.

In previous thesis work, by Francesco da Prato, the automation of the deposition of sealant material was done via robocasting, which involves the design and formulation of a GC2 based paste. Furthermore, he also studied alternatives to the metal used, Inconel 625. Robocasting had shown promising results and was therefore kept as the main deposition technique for subsequent sample preparations. An initial paste recipe was also developed and optimized via rheological characterization. Following Francesco da Prato's work, Thomas further developed the robocasting paste recipe and further optimized the printing parameters. Samples that involves the joining of LSCF membranes to Inconel 625 circular samples were prepared and studied, with comparisons made to the previous work in order to check for improvements. Thermal treatment was also further optimized, with the development of a thermal treatment curve specific to the developed paste in order to have a better joint. A drying step was also added before the thermal treatment which led to better adhesion of the paste to the metal. Tape casting was also studied as another deposition technique, which also involved the development of a GC2 slurry suitable for the preparation of a tape that can be directly placed on the metal. Samples prepared by robocasting showed good adhesion to both surfaces, but the issue of crack formation and pores persisted. For samples prepared by tape casting showed bad adhesion on the other hand.

The main objective of this work was the further optimization of the joining process, by further developing the thermal treatment curve, adjusting printing parameters for robocasting, and modifying the paste's recipes. Sealant deposition via robocasting was the primary focus, with tape casting also studied. In addition to LSCF single-

phase membranes, a newly developed membrane by RSE, 70CGO-30STF82 dual-phase membranes, were provided. Crofer 22APU metal samples were also provided to study as a potential metal support, and it could serve as a replacement to Inconel 625. During the thesis work, multiple samples were prepared in order to find the best combination of membrane and metal, where the joint showed the best properties, with joint testing performed to check for crack and pore formations.

2 Experimental Methods

2.1 GC2 Glass

During the thesis work, for the joining material between the metal and ceramic, a type of glass named GC2 was used. GC2 is a Ba-based borosilicate glass with minor amounts of CaO and Al_2O_3 . [8]

Precursors to weigh	Al_2O_3	H_3BO_3	SiO_2	BaCO_3	CaCO_3
wt%	3.90	9.39	31.40	48.71	6.65

Table 2.1: Composition of precursors used for GC2 glass formulation.

Table 2.1 shows the precursors used for making GC2 glass, which after being put in the same container, is put on a stand mixer for a period of at least 24 hours to ensure the mixture becomes homogeneous. Following the mixing step, the mixture was transferred to a platinum-rhodium crucible and placed in a furnace for the casting process. The furnace used was the Nabertherm 3000 due to its ability to reach very high temperatures which in this case is suitable for applications such as casting. The furnace was heated up to 1500°C at a rate of $5^\circ\text{C}/\text{min}$, then the crucible is put inside for a period of 30 minutes with the lid on followed by another 30 minutes without the lid.

During the first 30 minutes the lid is on to prevent any splatter outside of the crucible as a result of the chemical transformation occurring, during which CO_2 and H_2O are released, leading to the final composition of GC2 seen in Table 2.2. Following the casting process, the molten glass is poured quickly on a metal plate allowing it to cool down fast to room temperature. The end of the casting process can be seen in Figure 2.1, with the resulting glass after cooling in Figure 2.2.



Figure 2.1: Molten GC2 glass being poured on a metal plate at the end of the casting process

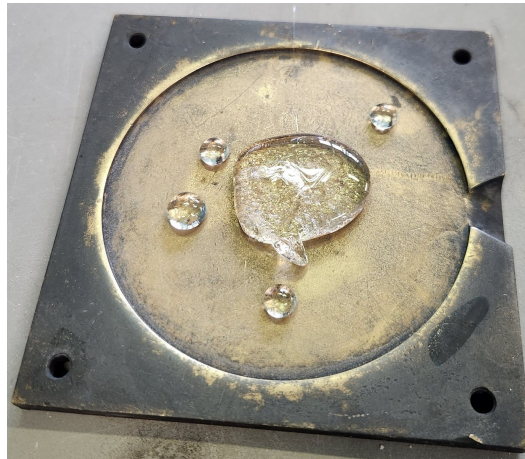


Figure 2.2: GC2 glass after cooling

GC2 Composition	Al_2O_3	B_2O_3	SiO_2	BaO	CaO
wt%	4.72	6.44	38.21	46.09	4.54

Table 2.2: Composition of GC2 glass.

BaO acts as the main network modifier, which affects greatly the CTE and wettability of the glass-ceramic that is derived from the glass. Based on measurements performed by Francesco da Prato, it is known that the CTE of GC2 glass is $10.88 \times 10^{-6} \text{ K}^{-1}$, the glass transition temperature (T_g) is around 670°C , and the crystallization temperature (T_x) is around 880°C . These temperature ranges are suitable given that the working temperatures are above 800°C .

2.1.1 Preparation of glass powder

In order to use the GC2 glass produced, it must first be pulverized into powder of particle size less than or equal to $25\mu\text{m}$. Small particle sizes of that range have many benefits when it comes to their use in robocasting. Their size allows for better dispersion in the paste medium, easier extrusion, and higher solid loading for paste formulations become possible [9]. To achieve this the glass must first be milled using a ball miller (see Figure 2.3) until the glass is turned into powder. Usually the first time milling the glass requires a higher amplitude to properly crush all the glass, given that they are initially large (in the range of millimeters). This is followed by a sieving process using a sieve (see Figure 2.4) for a period of around 30-40 minutes. The powder collected in the tray beneath the net can be saved for future use in pastes, while the powder still on the net can undergo another milling process at lower amplitude, before being sieved again.



Figure 2.3: Ball miller used



Figure 2.4: Sieve after usage

2.1.2 Particle Size Analyzer

After the sieving process, an analysis of the powder was performed using a Mastersizer 3000+ from Malvern Panalytical (see Figure 2.5). The goal of this analysis is to provide information about the particle size distribution in order to check the reliability of the sieving process.



Figure 2.5: Mastersizer 3000+ from Malvern Panalytical

This analysis uses the technique of laser diffraction. A little amount of powder is first mixed in distilled water, all placed in a 600ml glass beaker, through which a laser beam passes. The angular variation in intensity of the scattered light is measured,

with large particles scattering light at small angles, and small particles scattering light at large angles, both relative to the laser beam. Angular scattering intensity data are subsequently analyzed to determine the size of the particles responsible for the observed scattering pattern, and a volume equivalent sphere diameter is calculated [34]. In the case of this analysis in particular, it was made with 3.37% laser obscuration and without ultrasound.

2.1.3 Differential Scanning Calorimetry (DSC) test

To verify that the produced glass has the desired properties, a DSC analysis is needed. This test, which is performed on glass powder, measures the change of the material's heat capacity (C_p) with temperature. Based on the results, some characteristic temperatures points can be determined such as the glass transition temperature (T_g), and the crystallization temperature (T_x). The data can then be used to compare with previously tested glass powders in order to verify that the produced glass has the correct properties.

The instrument used for the measurement was the DSC 404 F3 Pegasus by Netzsch (see Figure 2.6). It consists of two small platinum–rhodium crucibles: one containing the sample and the other serving as the reference. The system also includes a furnace, a differential thermocouple used to measure the temperatures of both the sample and the reference, and a computer for data acquisition. During the measurement, the temperature difference between the sample and the reference material is converted into a heat flow signal that is calibrated to determine the heat absorbed or released by the sample. The instrument uses a feedback loop that maintains the sample at a constant temperature while continuously measuring the power required to achieve this condition with respect to the reference crucible. This configuration allows for precise temperature control and enables accurate determination of enthalpy changes and heat capacity, while also ensuring reliable isothermal measurements. The output of the analysis is presented as a DSC curve, where heat flow is plotted as a function of temperature. Thermal events occurring within the sample appear as peaks in the curve, with endothermic peaks corresponding to processes that absorb heat, such as the glass transition or melting, whereas exothermic peaks indicate heat release, typically associated with crystallization [35].



Figure 2.6: DSC 404 F3 Pegasus by Netzsch.

For the sample measurement, the sample crucible was loaded with around 30mg of GC2 powder at a heating rate of $5^{\circ}\text{C}/\text{min}$. During the experiment, an air flow of 50mL/min was maintained, while argon was supplied at 20mL/min as a protective gas. Before doing the sample measurement, typically in the day before, a reference correction measurement is taken with an empty sample crucible with the same parameters of the sample measurement test. A reference curve is then built which is later subtracted from the sample curve to give the true DSC curve of the GC2 glass.

2.2 Preparation of glass paste for robocasting

Provided that properties of the GC2 glass powder has been verified by the DSC test, the powder can then be mixed with other additives in order to create a paste that is suitable for making the glass-ceramic sealant. For the deposition of this paste, several techniques were developed to ensure controllable glass-ceramic thickness and a high level of reproducibility in the resulting joint. One of these techniques is robocasting, for which a specific paste formulation needs to be followed.

2.2.1 Ink Formulation

For ink printing via robocasting, the glass paste must have some specific rheological properties that will be elaborated later in this report. To achieve the desired properties

for this paste, the GC2 glass powder should be mixed with some organic compounds that will act as the solvent, plasticizer, and binder in this mixture, with the composition of the robocasting paste used for this thesis present in Table 2.3.

Material	Function	Amount
GC2 glass powder ($< 25 \mu\text{m}$)	Solid Load (SL)	x wt.%
Solvent and other additives (AS)		(100-x) wt.%
Terpineol	Solvent	AS - DPK_103 - PEG_400 - PVB
Disperbyk-103 (DPK_103)	Dispersant	2 wt.% SL
Polyethylene glycol 400 (PEG_400)	Plasticizer	50 wt.% PVB
Polyvinyl butyral (PVB)	Binder	5 wt.% AS

Table 2.3: General formulation for the robocasting paste prepared

In this paste, the solid load, which was the GC2 glass powder, present played a central role in influencing the viscosity of the paste and the porosity of the joint post-thermal treatment. This directly affected the thickness of the paste deposited on the metal support, with high viscosity meaning less spreading of the paste and therefore thicker joints. To avoid such issues with viscosity due to the high solid load, a dispersant, chosen to be disperbyk-103 from BYK Additives, was added to the mixture. Dispersants prevent particles from agglomerating and helps with their homogeneous distribution in the paste medium by adsorbing to the glass particle's surfaces in order to reduce interparticle friction and to also overcome van der Waals interparticle attractive forces, which, as a result, reduces the viscosity of the paste [9]. The binder acts as the additive responsible for creating bonds between the particles, which maintains their cohesion throughout all stages of the joining process. For this paste, polyvinyl butyral (PVB), a polymer with the chemical formula $(C_8H_{14}O_2)_n$, supplied by Sigma-Aldrich, was used as the binder. Another important additive is the plasticizer, chosen to be polyethylene glycol 400 (PEG-400) supplied by Sigma-Aldrich. Its main effect was to help reduce the viscosity of the paste and make it more flexible by reducing the yield stress of the paste, allowing it to easily flow through the nozzle during deposition. Terpineol, which is a mono-alcohol that was provided by Sigma-Aldrich, was selected as the solvent to dissolve all additives incorporated in the paste formulation. Due to its volatility, it was recommended that the paste be used within four days of its formulation to avoid changes in the paste's rheological properties. Furthermore, it should be noted that the portions of additives added is very important in order to allow their fast and effective burnout during the thermal treatment process, while preventing the formation of cracks [9].

By following all the mixing steps in Table 2.4, the formation of bubbles or clusters in the paste was avoided, which would have negatively affected the quality of the joint during the deposition process.

-
- 1 Determine amount of paste required.
 - 2 Weigh the needed amounts of Terpineol and Disperbyk-103.
 - 3 Mixing step in Thinky Mixer for 6 minutes at 1600 rpm.
 - 4 Add one third of the required GC2 glass powder to the mixture.
 - 5 Mixing step in Thinky Mixer for 6 minutes at 1600 rpm.
 - 6 Repeat steps 4 and 5 two additional times.
 - 7 Add the required amount of PEG-400 to the mixture.
 - 8 Mixing step in Thinky Mixer for 6 minutes at 1600 rpm.
 - 9 Add the required amount of PVB to the mixture.
 - 10 Mixing step in Thinky Mixer for 10 minutes at 1600 rpm.
 - 11 Defoaming step in Thinky Mixer for 4 minutes at 1400 rpm.
-

Table 2.4: Procedure used for the preparation of robocasting paste

2.2.2 Rheology Testing

To verify that the paste has rheological properties suitable for robocasting, some rheology tests were performed using MCR 302e by Anton Paar (see Figure 2.7), which is a parallel plate rotational rheometer. Rotational rheometers are precise instruments able to apply a wide range of shear stresses, shear strains and shear rates to a sample, by using specific geometrical configurations and by controlling the environmental conditions. The instrument consists of a lower stationary plate, where the paste is placed on using a spatula, and an upper adjustable plate that can rotate [31]. For the tests, they were done in ambient conditions with the distance between the upper and lower plates being 0.5mm.

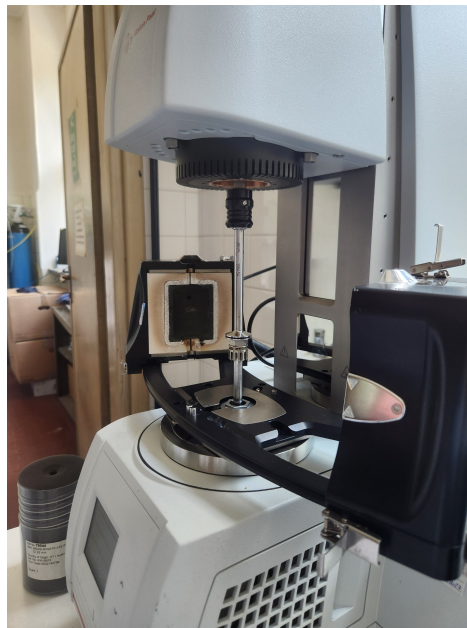


Figure 2.7: Rheometer used

The paste should be able to flow without resistance through the nozzle during the deposition process. Following the deposition on the metal, the paste should be able to hold its shape on the surface to avoid spreading. For checking these properties, two specific rheological tests are performed, which are the flow sweep test and the three interval thixotropy test (3ITT).

Flow Sweep Test

One desirable rheological property that the paste should have is shear-thinning behavior, which is characteristic of pseudoplastic materials, because due to decreasing viscosity with increasing shear rates a decrease in extrusion pressure occurs, allowing a smooth extrusion of paste through the nozzle used. With this relation between shear rate and viscosity present, a flow sweep test was used. This rotational test involves the application of an increasing shear rate and while this occurs, the change in viscosity was measured [31]. Additionally, the shear stresses are measured, which is placed in a separate graph than the one with viscosity. For this thesis work, the test was done for the shear rate range of 0 s^{-1} to 200 s^{-1} .

Three Interval Thixotropy Test (3ITT)

Another crucial rheological property that the paste should have fast shape recovery after deposition on the metal's surface, which would prevent the paste from spreading. In other words, it should have the ability to go from fluid-like flow during printing to solid-like behavior after deposition. A test that is suitable to study this behavior is the three interval thixotropy test (3ITT). From this test, the study of the change of viscosity over time can be used to verify if the paste exhibits thixotropic behavior, which is when the viscosity decreases over time as the results of progressive breakage of the internal attractive interactions due to the continues stress application during the printing process. This test allows mimicking an extrusion-based printing process by applying three consecutive steps with different shear rates. The first step simulates the paste's rest state in the nozzle, followed the the second step simulating the paste during printing, then the third step simulating the paste's rest state after deposition [31]. The shear rates used to simulate the rest states where assumed to be 3 s^{-1} , a value set previously by Thomas, and therefore they were used for this work, while the printing step simulation involved first the calculation of the maximum shear rates during printing. During extrusion, the maximum shear stresses are present at the walls of the nozzle where there is contact with the paste, and the maximum shear rate can then be calculated by (2.1):

$$|\dot{\gamma}|_{\max} = \frac{4\bar{v}}{R} \quad (2.1)$$

with R the radius of the nozzle, and $\bar{v}$ the printing speed [31]. For most samples prepared by robocasting, the printing speed used was 2mm/s, and therefore the shear rate was found to be 13.3 s^{-1} , while for the ink deposition during the final samples preparation a printing speed of 10mm/s was used, leading to a maximum shear rate of 66.7 s^{-1} . During this test, the shear rates used were 3 s^{-1} , 15 s^{-1} , and 3 s^{-1} for the three steps respectively. For the test performed towards the end of the thesis work, the second interval's shear rate was changed to 70 s^{-1} in order to better simulate the paste under the conditions of the higher printing speed used for preparing the samples that were sent to RSE. It should be noted that the selected value for the shear rates for the second interval of the 3ITT are higher than the calculated value but still close to the values found, which is what is required for the test to be as accurate as possible [31].

The goal of this test was to verify that the recovery of the solid-like behavior is fast enough to retain the nozzle shape and if the restored modulus is high enough to ensure a good printing fidelity and the self-supporting capacity of the printed structure. Furthermore, the verification of the thixotropic behavior of the paste, given that typically glass pastes exhibit such behavior, is also an important aspect [31].

2.2.3 Ink Deposition

In this thesis work, the Zmorph VX 3D printer from Zmorph was used for the paste deposition. The ink printer was fitted with a specialized thick-paste extrusion system consisting of a stepper motor driving a piston mechanism. This setup enabled the material to be dispensed through a 1.2 mm nozzle with a high degree of consistency and control. In addition, the tool head was adapted to hold a 5 ml syringe, which further improved the precision of the extrusion process and allowed for finer regulation of material flow during printing.

Before starting any ink deposition process, a printing profile was first prepared and uploaded onto the software of the 3D printer. A 2D model consisting of a straight line with a length of 15mm and a separate circle of 18mm diameter was prepared using Autodesk's AutoCAD software (see Figure 2.8). The initial printed line is present in order to start the ink extrusion before the actually deposition takes place in order to ensure a smoother deposition on the metal sample.



Figure 2.8: Model on AutoCAD

This model was subsequently saved in the .dwg and .dxf file formats. The .dxf file was then imported to Voxelizer 3.0, a software developed by Zmorph. Using this software, the printing parameters were adjusted and then the file was saved as a .gcode file, which is a readable format by the Zmorph VX 3D printer software. On Voxelizer 3.0, the printing parameters are the following, where the layer count determines how many layers are deposited over a printing path, which in this case is set to 1 due to it being 2D printing. Furthermore, layer height determines the height of the nozzle above a set reference, the path width dictates the volume of extruded material, and the print speed sets the tool head's travel rate. Print speed is important to have the most ideal printing profile, with the best values being in the range from 2mm/s to 10mm/s, as recommended by Francesco da Prato. For most samples that were produced during the thesis work, the parameters used are the ones in Figure 2.9. However, for the samples made at the end of the thesis work, specifically those sent to RSE, the parameters were changed to the ones in Figure 2.10. Justification for the changes made to the printing parameters are provided later in this report.

Layer count	1
Layer height	2 mm
Path width	5 mm
Travel speed	120 mm/s
Print speed	2 mm/s
Retraction	☒
Retraction height	3 mm
Retraction amount	4 mm
Retraction speed e	10 mm/s
Retraction min distance	0 mm
Extra length on restart	0 mm

Figure 2.9: Voxelizer printing parameters used for most samples

Layer count	1
Layer height	2 mm
Path width	25 mm
Travel speed	120 mm/s
Print speed	10 mm/s
Retraction	☒
Retraction height	3 mm
Retraction amount	4 mm
Retraction speed e	10 mm/s
Retraction min distance	0 mm
Extra length on restart	0 mm

Figure 2.10: Voxelizer printing parameters used for samples produced for RSE

The .gcode file was then uploaded to the software of the 3D printer. Before the printing process can begin, the tool head must be properly prepared and installed with a 5 ml syringe pre-filled with the paste. After being mounted, the syringe was correctly positioned and securely aligned to ensure stable operation and accurate material deposition during printing. Following the setup of the tool head, and placement of the metal samples on the platform of the machine, the program was selected and initiated. Figure 2.11 shows an instance of robocasting being performed to deposit a paste on a sample.



Figure 2.11: Robocasting process in progress.

2.2.4 Profilometer Analysis

After the ink deposition and drying steps were completed, a profilometer was utilized to check the geometry of the paste deposited. The machine used was Intra Touch Ultra by Taylor Hobson (see Figure 2.12). The goal is to measure the width and thickness of the deposited and dried paste on the metal, which would later be compared to the width and thickness of the paste following the joining of the metal to the OTM.

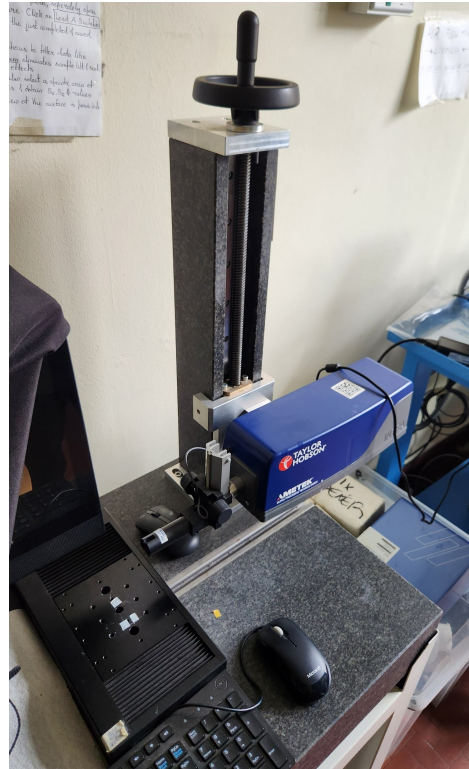


Figure 2.12: Intra touch Ultra by Taylor Hobson

This device uses a stylus, with a finely pointed probe and a measuring head, that is mounted on a gauge that is connected to a unit that is used to finely adjust the height of the probe. It maintains constant contact with the object being analyzed at all times while maintaining a constant contact force. Following the placement of the metal with the dried deposited paste, the stylus height and position was carefully prepared before initiating the measurement. In the case of this measurement, the stylus had to move in only one direction in order to measure both thickness and width of the deposited paste, with this process repeated multiple times on multiple sides of the deposition in order to determine the average dimensions. Data analysis was performed as a last step in order to remove any noise from the profile measurements.

2.3 Preparation of glass paste for tape casting

Another technique for glass deposition was tape casting. The goal was to make a paste, and using a doctor blades, it was spread over a sheet of silicon-coated mylar and left to dry in order to get a tape, or in other words, a thin layer of glass powder held together by additives that can readily be shaped and cut before being directly placed on the metal. As for robocasting, the paste has to follow a specific paste formulation.

2.3.1 Ink Formulation

The paste formulation for tape casting follows a very similar procedure to that of the robocasting paste. Unlike in robocasting, the paste produced should have lower solid load and therefore lower viscosity. With the goal of having an easily spreadable paste that has the ability to dry fast in room temperature, resulting in a glass tape that can later be cut and placed on the metal support, ethanol was used as a solvent alongside with terpineol. Ethanol cannot be used alone due to its high volatility, which would have resulted in a tape that breaks apart due to its very fast evaporation rate. Terpineol was therefore mixed with the ethanol to reduce the volatility. Table 2.5 shows the general formulation used for making the tapes via tape casting.

Material	Function	Amount
GC2 glass powder ($< 25 \mu\text{m}$)	Solid Load (SL)	x wt.%
Solvents and other additives (AS)		$(100 - x)$ wt.%
Terpineol	Solvent	Total solvent mixture $- 0.9 \times \text{PVB} - \text{Ethanol}$
Ethanol	Solvent	16 wt.% Total solvent mixture
Disperbyk-103 (DPK_103)	Dispersant	1 wt.% SL
Polyethylene glycol 400 (PEG_400)	Plasticizer	50 wt.% PVB
PVB (Polyvinyl Butyral) 10% solution	Binder	10.5 wt.% AS $\times 10$

Table 2.5: General formulation for the tape casting paste produced

Like in the paste preparation for robocasting, the procedure for prepare the paste for tape casting followed the same mixing steps, with the only change being that there is ethanol added with the terpineol and the disperbyk-103 in the first mixing step as seen in Table 2.6.

2.3.2 Tape casting process

Following the preparation of the paste, the next steps followed required the usage of a doctor blade and a tape caster. The idea was to spread the paste on a silicon-coated mylar that had been placed on the tape caster via a doctor blade. For ensuring that the tape has the correct properties of thickness and homogeneous distribution of the

-
- 1 Determine amount of paste required.
 - 2 Weigh the needed amounts of Terpineol, ethanol and Disperbyk-103.
 - 3 Mixing step in Thinky Mixer for 6 minutes at 1600 rpm.
 - 4 Add one third of the required GC2 glass powder to the mixture.
 - 5 Mixing step in Thinky Mixer for 6 minutes at 1600 rpm.
 - 6 Repeat steps 4 and 5 two additional times.
 - 7 Add the required amount of PEG-400 to the mixture.
 - 8 Mixing step in Thinky Mixer for 6 minutes at 1600 rpm.
 - 9 Add the required amount of PVB to the mixture.
 - 10 Mixing step in Thinky Mixer for 10 minutes at 1600 rpm.
 - 11 Defoaming step in Thinky Mixer for 4 minutes at 1400 rpm.
-

Table 2.6: Procedure used for the preparation of robocasting paste

paste, the program of the tape caster was set to allow the movement of the doctor blades along the mylar at a speed of 5mm/s, while the doctor blades were tuned to the desired height in the scale of micrometers. In this thesis work, the tape caster used was the TQC Sheen tape caster (see Figure 2.13).

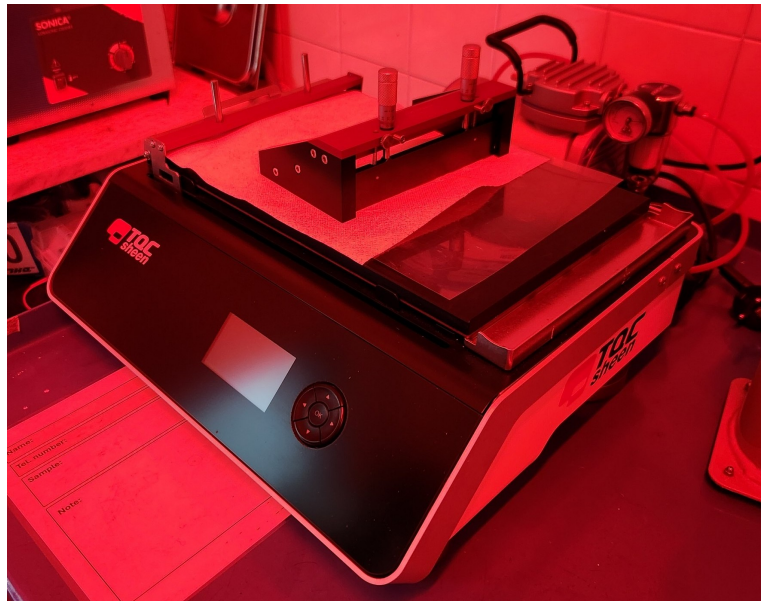


Figure 2.13: TQC Sheen tape caster and doctor blades (on top)

After spreading the paste on the mylar, the paste was left to dry for a period of approximately two days under a fume hood. The resulting tape could then be removed and cut to the desired shape, which in the case of this thesis work was a ring shape, after which it can be placed on the surfaces of metals used for making the samples. Figure 2.14 shows the an example of metal (Inconel 625) samples with tape shaped and placed on them before a joining process with LSCF membranes were initiated.



Figure 2.14: Metal samples with tape placed on them before joining process.

2.3.3 Thermogravimetric Analysis (TGA)

Before any joining was performed with a tape casted joint, a thermal treatment curve had to be designed first. To do so, a thermogravimetric analysis (TGA) had to be performed on a tape. TGA is a type of thermal analysis where the mass of a sample, placed inside a high temperature furnace, is monitored over time as the temperature changes [36]. Its goal in the cases of this thesis was to determine the temperature points where the different additives present in the paste evaporate the fastest, and based on these temperature points, a stepped thermal treatment curves would be designed. For the thesis work, the TGA was performed using STARE System TGA/DSC 3+ by Mettler Toledo (see Figure 2.15).



Figure 2.15: Machine used to perform TGA

For the sample, a small amount of a tape that had previously been prepared by Thomas, called tape V3 with a solid load of 67%, was chosen to be analyzed.

2.4 Sample Preparation

Sample preparation is a critical step that requires following a series of steps in order to guarantee a successful joining process. Throughout this thesis, many samples were prepared and tested, with the ultimate goal of having 3 samples sent to RSE for further testing.

2.4.1 Preparation of components for joining

The preparation of samples involved a series of steps that had to be taken in a specific order. Circular metal samples with dimensions of around 20mm of both Inconel 625 and Crofer 22 APU were provided by RSE. In the case of Crofer 22 APU, the metal had to first undergo a pre-oxidation step in a furnace (Carbolite 1300, see Figure 2.17) at 900 °C for 2 hours. As a result of this step, a layer made of chrome manganese oxide forms on the surface, which is characterized with great thermodynamic stability and good electrical conductivity [13]. This was required for Crofer 22 APU due to the failure of joints during thermal aging tests performed by RSE when the metal was joined without pre-oxidation due to the migration of chromium from the metal into the adjacent surface of the glass-ceramic sealant. After the preparation of the metal samples, deposition of the glass-ceramic layer was done either by robocasting or tape casting. For robocasting, a drying step followed the deposition step, where the sample was placed into a low temperature furnace at 80 °C for 20 minutes in order to induce the evaporation of the solvent (terpineol). Drying was needed to prevent the spreading of the paste on the surface of the metal when the OTM is added on top of the paste. Depending on the type of metal used, an OTM was then placed carefully on top, with its dense side facing the sealant layer, followed by the addition of weights, which were discs of Inconel 625 with diameters of around 40mm. In order to ensure that the applied pressure on the glass paste layer is suitable for an effective joining to both membrane and metal, the masses placed on top of the membranes ranged from 70-73g, leading to the application of a pressure in the range of 12.2-12.7kPa, which is within the desirable range of 10-20kPa. LSCF single phase membranes were used with Inconel, while for Crofer 22 APU, 70CGO-30STF82 dual phase membranes were utilized. Finally, a thermal treatment process was performed on the samples. Figure 2.16 shows two samples inside the Carbolite 1300 furnace with the Inconel 625 plates placed on top before the thermal treatment is initiated.



Figure 2.16: Samples placed inside of Carbolite 1300 furnace with weights placed on top before thermal treatment process was initiated.



Figure 2.17: Carbolite 1300 furnace.

2.4.2 Thermal Treatment Procedure

Following the sample preparation steps, the samples were placed in a high temperature furnace, Carbolite 1300, to undergo thermal treatment, a crucial step that was required to ensure an effective resulting joint. The main goals were to lead to the evaporation of the additives in the glass paste, and to make the glass soften to achieve

wetting of both metal and OTM surfaces that are in contact. Careful control of both heating and cooling rates were needed to reduce the amount of pores that result from the evaporation of the additives and to avoid the formation of cracks due to the presence of residual stresses, especially during the cooling process. During the thesis work, different thermal treatment curves were developed for when either robocasting or tape casting was used. For the samples that involved robocasting for glass deposition, two thermal treatment curves were used, as seen on Figures 2.18 and 2.19.

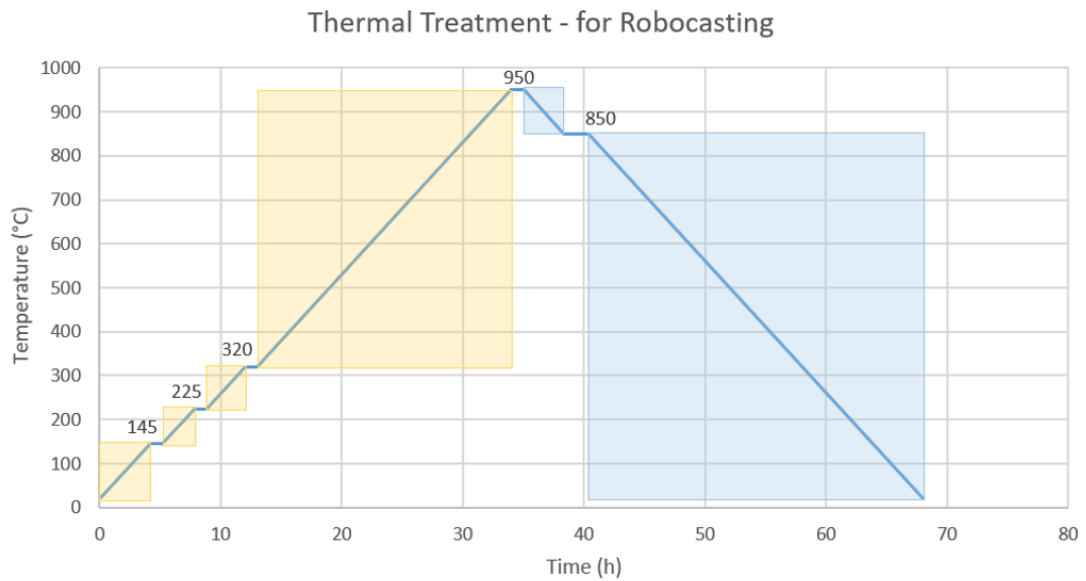


Figure 2.18: Thermal Treatment curve with a heating rate of $0.5^{\circ}\text{C}/\text{min}$ and a cooling rate of $0.5^{\circ}\text{C}/\text{min}$

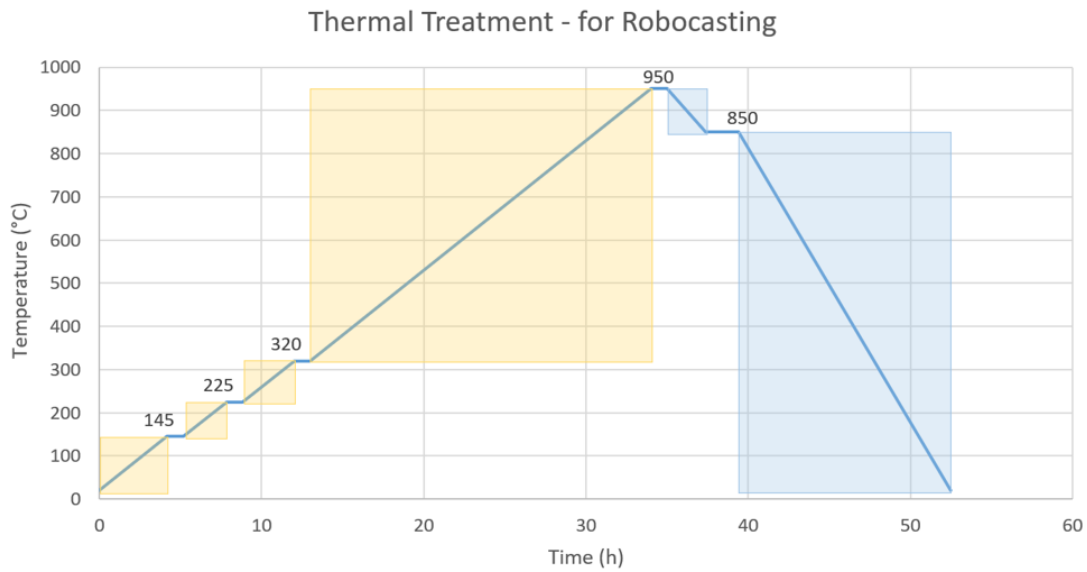


Figure 2.19: Thermal Treatment curve with a heating rate of $0.5^{\circ}\text{C}/\text{min}$ and a cooling rate of $0.7^{\circ}\text{C}/\text{min}$

Figure 2.18, which took around 68 hours, was first used at the start of the thesis work, but was eventually changed to the thermal treatment on Figure 2.19 to shorten the time needed. It should be noted that the thermal treatment used to prepare the samples that were delivered to RSE for leakage and thermal aging tests were made using the thermal treatment curve of Figure 2.18. To achieve an effective evaporation process for the additives, the thermal treatment involved dwells of 1 hour each at three different temperatures during the heating step. The first dwell at 145°C aimed at evaporating the solvent, Terpeneol, followed by the second and third dwells at 225°C and 320°C for removing the dispersant, Disperbyk-103, and the binder, PVB. According to Francesco Da Prato, at the peak of 950°C , a dwell of 1 hour was needed to achieve optimized wettability of both surfaces in contact, and to also promote maximum sintering of the glass powder and its optimal densification. After the heating steps were completed, the cooling step to room temperature was done, with one dwell at 850°C for 2 hours, a temperature that was chosen as it sits between the onset temperature of crystallization of GC2 and the crystallization temperature, T_x . During this dwell, growth of crystalline phases (Sanbornite) occur, which was important to achieve the desired thermomechanical properties for our application.

In the case of a joint made by tape casting, a different thermal treatment curve, see Figure 2.20, was developed based on the results of the TGA analysis performed on tape V3 that was previously made by Thomas, with these results to be explained later in this report. The reasoning for the choice of heating and cooling rates, and for adding

the dwelling steps follow the same logic as for the joint produced via robocasting. The main difference present is that there were four dwelling steps at different temperatures during the heating step.

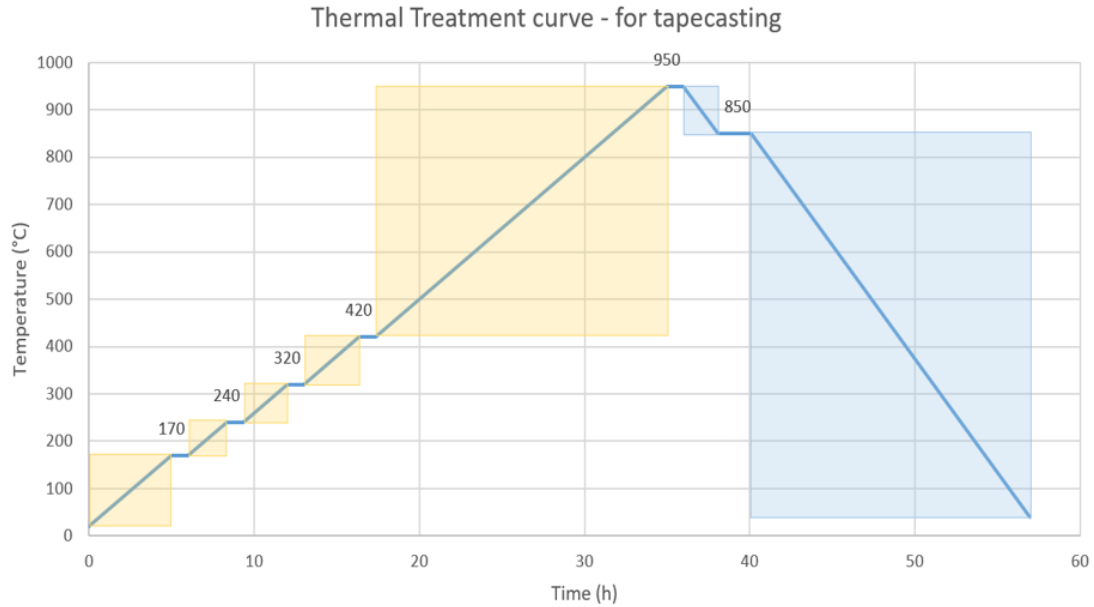


Figure 2.20: Thermal Treatment curve with a heating rate of $0.5^{\circ}\text{C}/\text{min}$ and a cooling rate of $0.8^{\circ}\text{C}/\text{min}$

2.5 Sample Testing

Provided that the samples were joined successfully following the thermal treatment, a series of steps were taken to check the quality of the joint and to detect defects that were present. This was important as it helped show what could be improved or changed during the sample preparation steps.

2.5.1 X-Ray CT-Scan

A computed tomography scan (CT-Scan) test is a non-destructive test that can be used to detect any internal defects in an object. For this thesis, it was used to detect any potential cracks, pores or voids that formed during the thermal treatment process in the joint. The machine utilizes an X-Ray source and a detector array. After placement of the sample in a sample holder in front of the X-Ray source, X-Rays are projected through the sample, and at a certain distance behind the sample a detector array is present. During operation, the sample holder slowly rotates allowing the detector array to measure the transmitted X-Rays intensities at each angle, which

allowed for the production of projection images. This was repeated until a full rotation was achieved, after which using a computer program, a high-resolution reconstructed three-dimensional projection of the samples were recreated. With a projected image, it was possible to view through the sample. Cross-sectional views both perpendicular and parallel to the joint were needed to determine the presence of defects and to verify that the quality of the joint at the metal and OTM interfaces were acceptable.

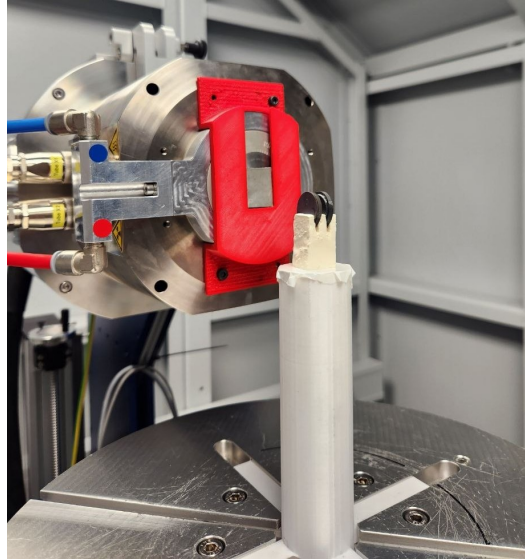


Figure 2.21: CT-Scan in J-tech laboratory with 2 samples fitted in the sample holder

It should be noted that the CT-Scan test was only done for some samples and not all, with it being more crucial for the samples prepared for RSE as they required non-destructive testing.

2.5.2 SEM test

Scanning Electron Microscopy (SEM) tests are used to investigate surface morphology and to study the micro structure of materials at high magnifications and resolutions. This allowed for the detection of micro-pores and cracks that potentially form during the thermal treatment. The technique utilized a focused electron beam to scan the surface under study. During operation, electrons were emitted from an electron source and focused onto the sample through a system of electromagnetic lenses. With the sample positioned on a movable stage, is scanned systematically in a raster pattern. As the incident electron beam interacted with the sample surface, multiple signals were generated, which included secondary electrons, back scattered electrons, and characteristic X-rays. These signals arise from different interaction mechanisms and provide complementary information regarding the material's morphology, surface

texture, and composition. The emitted signals were collected by specialized detectors and processed to generate high-resolution images, which allowed for detailed analysis of the material's structural and compositional properties.

Before a sample is tested using a SEM, a series of steps must first be taken. The steps that follow are destructive and were therefore not done on the final samples that were prepared and sent to RSE. First, samples were taken and engulfed in resin, after which they were left over night to allow the resin to harden. This step preceded the cutting step because the hardened resin prevents cracks from forming on the membrane during the cutting process, during which the sample is cut in half in order to expose a section view of the metal and OTM along with the glass-ceramic joint. After cutting, one section was polished progressively, beginning with coarse polishing paper and gradually proceeding to finer grades to ensure a well-polished cross-sectional surface. A final preparation step involved metallization, where the polished sample was taken and coated with a 7nm layer of platinum via sputter deposition. Metallization was essential to improve the electrical conductivity of non-conductive regions, such as the OTM and the joint layer, thereby enabling effective SEM analysis. Non-conductive sections, if uncoated, could trap incident beam electrons on the surface and result in bright spots in SEM images. Furthermore, excessive charge accumulation may result in localized heating, potentially causing surface degradation or damage to the sample [37]. An example of a sample prepared for SEM analysis can be seen in Figure 2.22.



Figure 2.22: Sample prepared for SEM testing.

Provided that all steps were undertaken, the samples were then mounted inside the SEM machine and imaged at high magnification following setting adjustments done on the software belonging to the SEM, with each sample tested separately. For this thesis, SEM JEOL JCM-6000Plus was used (see Figure 2.23).



Figure 2.23: SEM JEOL JCM-6000Plus

2.5.3 Leakage and Thermal Aging testing

For the three samples that have been prepared for RSE, only CT scanning was done on them as it was a non-destructive test. These samples were then packaged and sent to RSE (Ricerca sul Sistema Energetico) company for thermal aging and leakage testing, in order to study the ability of the joint to withstand prolonged periods at elevated temperatures with minimal gas leakage. Leakage testing aimed at verifying the gas tightness of the joint, where cracks and pores could lead to lower effectiveness in the hermeticity of the joint. For thermal aging, it was initially done for a period of one week, followed by two weeks if the sample survived the first week, and so on, with the test temperature set at 800 °C, in order to avoid the relaxation of the glassy phase in the glass-ceramic sealant.

Due to time limitations, the results of both tests were not provided on time by RSE.

3 Results and Discussion

3.1 GC2 Powder Test results

Throughout the thesis work, six separate batches of GC2 glass were prepared. For each batch an average of 50 grams of glass were cast which were subsequently milled and sieved to get the required glass powder for use in making the pastes for robocasting and tape casting purposes. As previously explained, the produced powders were then tested to verify that the glass powder made met the required properties for usage.

3.1.1 Particle Size Analyzer Test results

The results of the tests that were performed on GC2 glass powder batches 1 and 2 showed that 87.03% and 84.17%, respectively, of the sieved powder were smaller than $27.4\text{ }\mu\text{m}$. An explanation for the 12.97% and 15.83% of batches 1 and 2, respectively, that were larger than $27.4\text{ }\mu\text{m}$, can be that some sides of the particles, which were not spherical, passed through the pores of the sieve through their shorter sides. Another possibility could be that some of the particles that passed through the pores of the sieve agglomerated together during the test. With these assumptions it can be considered that the results are good.

In Figure 3.1, the results of both tested batches are summarized in a graph that shows the volume density percentage with particle size in micrometers represented in a logarithmic scale, with $25\text{ }\mu\text{m}$ marked with a dashed line. Based on the results, it was found that the peaks for the particle size distributions of both batches lay below $25\text{ }\mu\text{m}$, with the peak being in the range of $16.4\text{ }\mu\text{m}$ and $18.7\text{ }\mu\text{m}$ for batch 1, and for batch 2 in the range of $21.2\text{ }\mu\text{m}$.

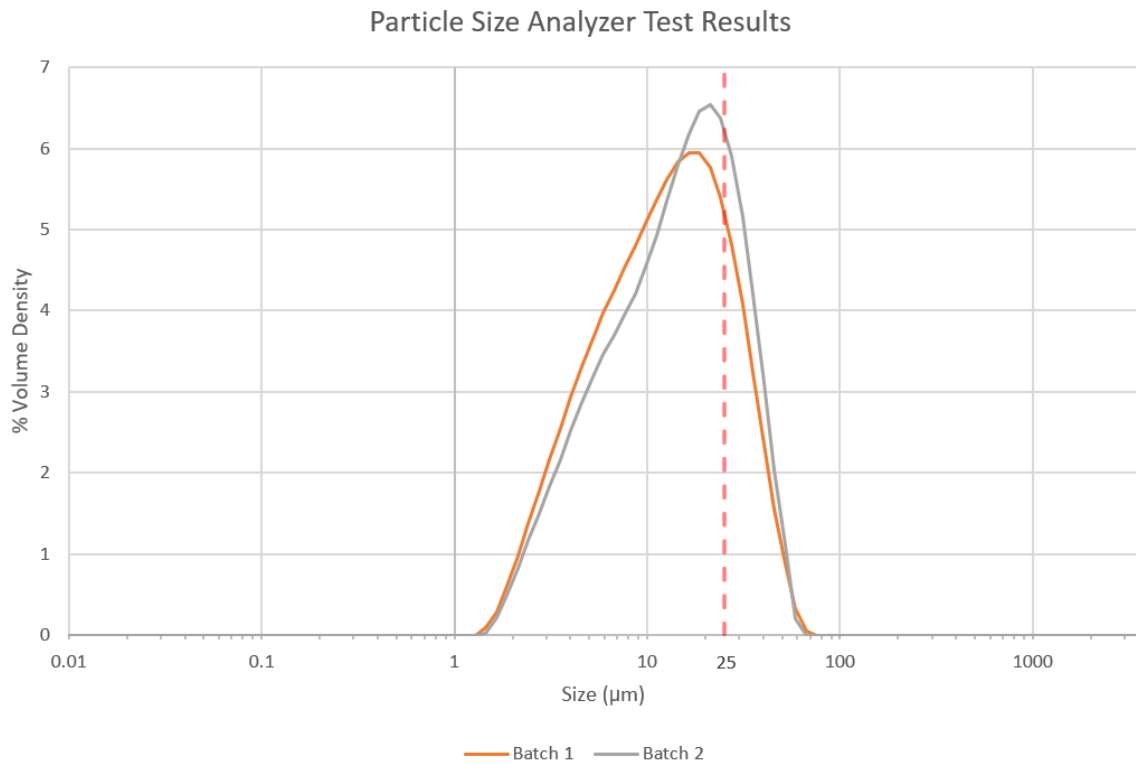


Figure 3.1: Particle Size Analyzer test results for sieved GC2 batches 1 and 2

Based on the results, it was verified that the sieving process was sufficient in separating the correctly sized particles from the milled batch. Due to time constraints, the test was not performed on other GC2 batches produced, but it should be expected that the results would come out similar to those of batches 1 and 2, due to the usage of the same sieve and ball miller throughout the thesis work.

3.1.2 DSC Test results

The DSC test was done on all batches prepared in order to verify their properties, with focus on detecting the glass transition temperature (T_g) and the crystallization temperature (T_x), which is where the crystallization process reached its maximum energy. As a point of reference, Francesco da Prato found that the T_g for GC2 glass was around 670°C and the T_x was around 880°C . Due to some calibration error of the DSC machine, not all results were included, and with time limitations, the inaccurate measurements were not repeated. Focus is placed on the measurements done for the 4th and 5th batches of GC2 glass that were prepared, with their results shown on Figure 3.2.

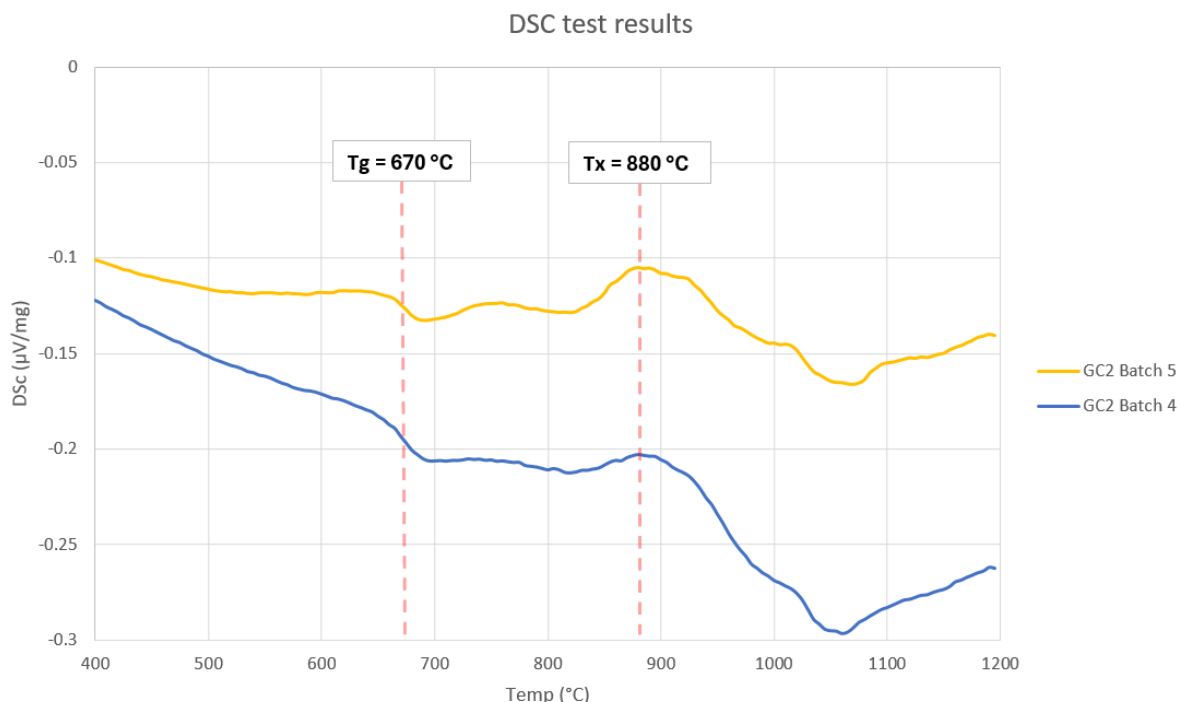


Figure 3.2: DSC test results for sieved GC2 batches 4 and 5

With reference to the graph, T_g was determined to be $670\text{ }^{\circ}\text{C}$ for both batches by finding the midpoint of the baseline shift on the DSC curve. The temperature value was calculated using the DSC software's program, where the temperatures at both the onset and the end of the baseline shift were first calculated before the midpoint temperature, T_g , was extrapolated. Below T_g , the glass is a solid amorphous structure with a lower heat capacity (C_p), where any heat provided to the glass in the temperature ranges below T_g is used to increase the vibrational motion of the atoms. At temperatures above T_g , the molecules gain the ability to move, allowing the glass to flow, with additional energy needed to support the movement of the atoms. Consequently, the C_p increases, which leads to a shift of the baseline on the DSC curve. In the case of T_x , it was determined to be around $880\text{ }^{\circ}\text{C}$ for both batches by finding the exothermic peak on the curve. Crystallization is an exothermic event, as heat is released during the rearrangement of the disordered molecules that are at a higher energy state into a highly ordered, crystal phase that is at a lower energy state. Therefore, as a result of the change in the energy states from a higher to a lower one, the excess heat is released, leading to an exothermic region on the DSC curve, in which the peak is where the highest rate of crystallization occurs.

The results found by the DSC analysis showed that a dwell at $850\text{ }^{\circ}\text{C}$ of 2 hours during the thermal treatment process is useful. At that temperature, which is below the crystallization peak but after the onset of crystallization, the growth of crystalline

phases, specifically Sanbornite, can be controlled, which provides the glass-ceramic sealant its desirable thermomechanical properties.

3.2 Robocasting Paste Rheology

Before arriving to the latest paste formulation, based on which the final samples were prepared for RSE, the paste underwent various changes. Specifically, the changes targeted the solid loading of the paste, which had a central effect on the viscosity of the paste. Rheology testing was done to verify the paste's required properties, such as shear-thinning and thixotropic behavior, and based on the tests, changes were applied to the solid load. As explained previously in this report, the two main tests involved were the flow sweep test and three-interval thixotropy test (3ITT).

Initially, the paste was made with 82.5% solid load (see Table 2.3 for ink formulation), based on the most optimal paste formulation found by Thomas. Therefore, to act as a reference for comparison, the results for Thomas' pastes with the formulation 82.5% are included in the graphs for the tests done. Furthermore, Thomas also tried using a paste with 84% solid loading, but due to less optimal results it was abandoned. Nevertheless, the results found for the paste with 84% solid loading is also included.

3.2.1 Flow Sweep Test results

The flow sweep test was mainly done following changes to the solid load percentage of the DIW paste. This was because a solid load change directly influences the viscosity of the paste, where an increase in the solid loading causes an increase in viscosity and vice versa. The flow sweep test measures both viscosity and shear stresses as a change in the shear rate is imposed, with the results separated into two separate graphs.

Figure 3.3 shows the graph of viscosity versus shear rate, with the shear rate measured from $0\text{--}200\text{ s}^{-1}$. On the graph, the results include two measurements previously made by Thomas for pastes with the solid loads of 82.5% and 84%, and three measurements performed by me, for pastes with a solid loading of 82.5% and 80%. Two of my measurements were done for the same paste formulation at different stages in the thesis work due to a change performed to the printing parameters, which led me to perform another set of rheology tests including a flow sweep test for completeness purposes. Thomas's measurements acted as reference to measurements that were performed during this thesis work in order to compare results.

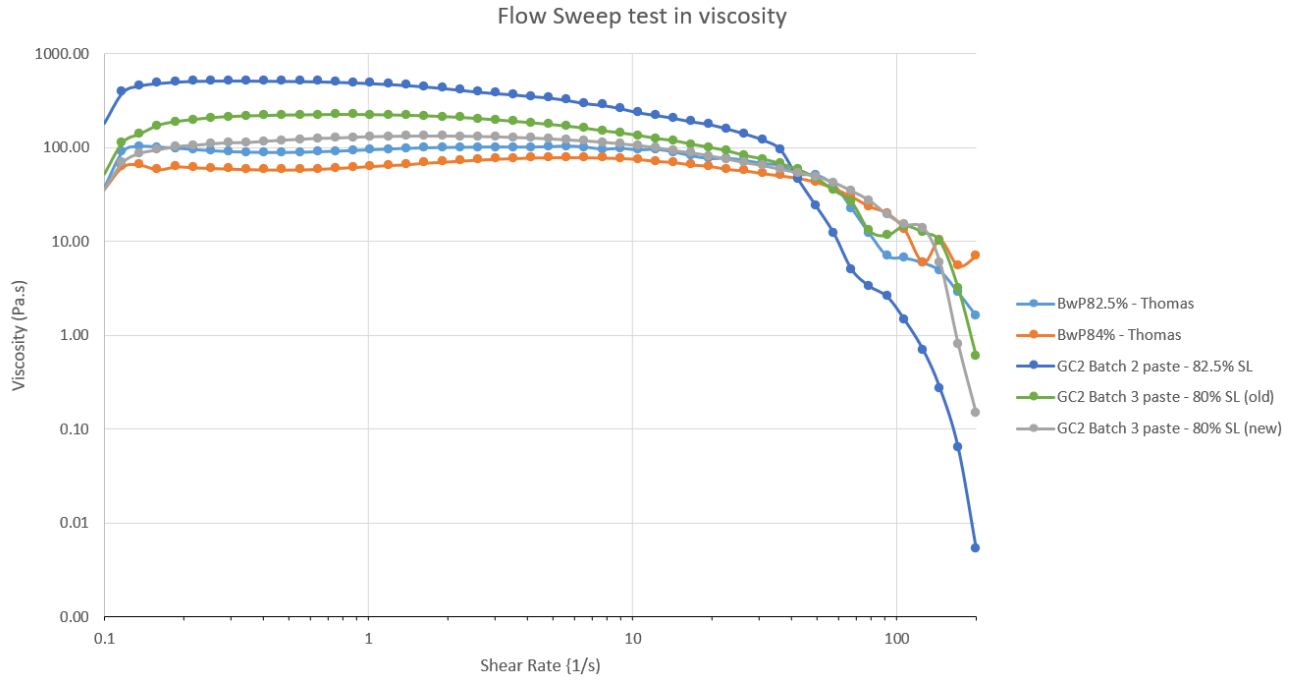


Figure 3.3: Flow sweep test results showing viscosity versus shear rate.

As expected, all pastes produced had a shear-thinning behavior, in which the viscosity reduces with an increase in shear rate. Shear-thinning behavior is favorable as it enables the paste to flow easier as the application of pressure during robocasting causes a reduction in viscosity and therefore easier printing. Between Thomas's pastes, the one with 82.5% solid load was deemed more favorable than the one with 84% solid load due its overall more optimal results in all rheology tests performed. Therefore, the paste was reproduced with 82.5% solid load for some sample preparations and tested in order to check its rheological behavior. Although it showed shear-thinning behavior, its viscosity was deemed too high, both visually and by measurement, with issues visible during the robocasting process that led to difficulty in having a perfectly circular deposition profile. An explanation for the difference between the viscosity of this paste and the one previously produced by Thomas can lie in the difference in ambient temperatures during the measurements done by Thomas previously. The 82.5% solid load paste was produced one more time in another sample preparation procedure, but was not tested by the rheometer, although its viscosity was still visibly too high visually. Hence, it was decided to reduce the solid loading to 80% for the following samples. Viscosity dropped as result, as seen on the graph, and the shear-thinning behavior remained, making it a more optimal paste for robocasting. Additionally, another paste with 80% solid load was tested following its usage in preparing one of the samples prepared for RSE, with its measurement showing a lower viscosity than the

measurement of the previous 80% solid load paste. This difference in viscosity can be attributed to a difference in particle dispersion between the two pastes or testing environment, as the ambient temperatures were slightly different between both testing dates.

Figure 3.5 shows the graph of shear stress versus shear rate, with the shear rate measured from $0\text{--}200\text{ s}^{-1}$. The measurements present are the same as in the previous graph. All curves show an increase in shear stress with an increase in shear rate, until a peak is reached, after which a drop is noted. This drop in shear stress can be attributed to a weakening in the network holding the particles in the paste and is characteristic to pastes that have a thixotropic behavior, where a drop in the applied extrusion pressure and therefore the shear stresses due to a reduction in the paste's viscosity allows for an easier printing process. Furthermore, all curves show shear thinning behavior, also referred to as pseudoplastic behavior with reference to the graph showing different classifications of viscous fluids in Figure 3.4.

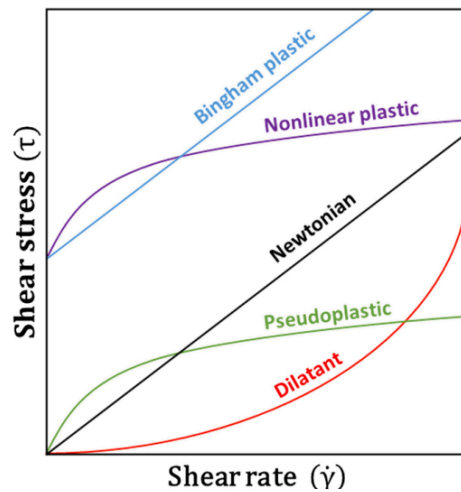


Figure 3.4: Different classifications of viscous fluids based on shear stress versus shear rate [31].

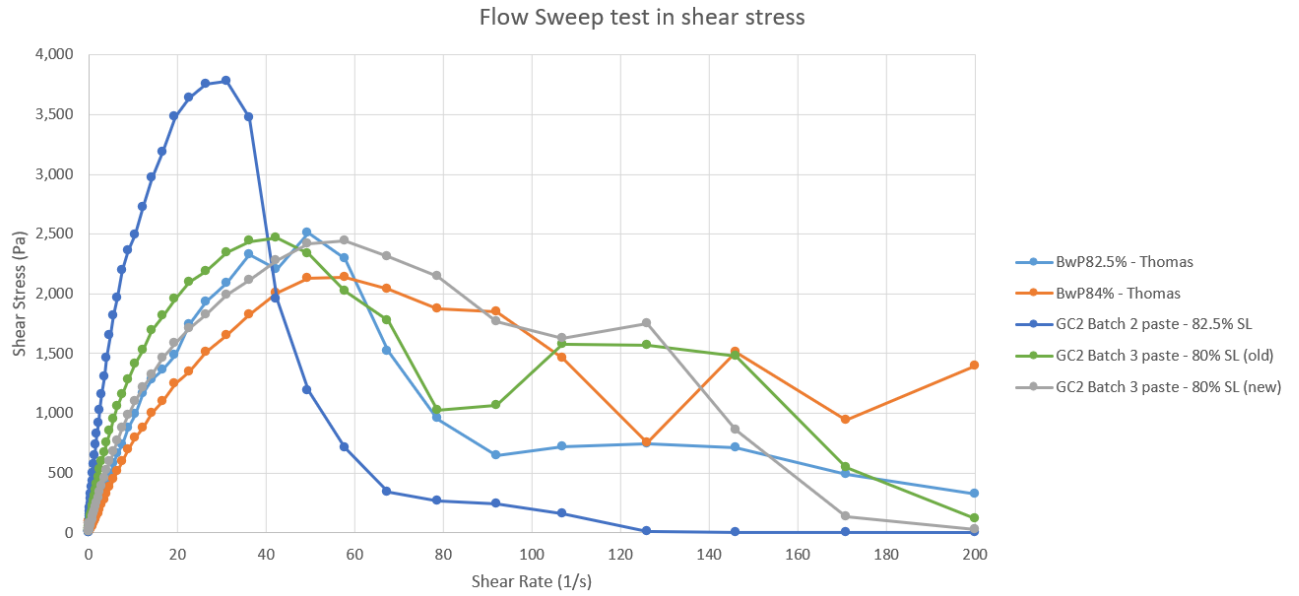


Figure 3.5: Flow sweep test results showing shear stress versus shear rate.

Between Thomas's pastes, the one with 84% solid load shows the lowest initial slope and the lowest stress reduction following the peak, implying that the paste's network is overall more resistant to structural breakdown due to its high solid load. For Thomas's paste with 82.5% solid load, a higher slope and peak is noted, with larger stress drop visible, meaning it has better shear-thinning properties. As mentioned before, this influenced the decision to start with a paste of 82.5% solid load, as it shows overall better properties than the one with the 84% solid loading.

The paste with 82.5%, which was reproduced for this thesis work, showed a much higher stress peak, with an extreme stress drop following it. During robocasting, it was noted visually how it was difficult to extrude given the printing parameters used, leading to an uneven annular profile, which was due to the high viscosity of the paste. This stress measurement with shear rate further confirmed that a paste with this solid load percentage was not the most optimal, and therefore the solid loading was reduced to 80%. Taking note of the green curve, belonging to the paste with 80% solid load that was produced earlier in the thesis worked before any changes were applied to the printing parameters, it can be seen that the shear stress peak is much lower than that of 82.5% solid load, with a less drastic drop in stress at high shear rates. Similarly, when the paste was reproduced later for the preparation of the RSE samples with 80% solid load, on the graph see the gray curve, a similar stress peak is noted, albeit at a high shear rate range. Both pastes with 80% solid loading showed a good shear thinning behavior, which is desirable for robocasting. It should be noted that the difference between both pastes in terms of both the position of the stress peak, and how the

stress reduces as the shear rate increases can be explained by the dispersion quality and the interactions between particles in the network during the test conditions, which were slightly different due to the ambient temperature in the room between both testing dates.

3.2.2 3ITT results

Similar to the flow sweep test, the 3ITT was done for each change in the paste's formulation. An additional reason for the measurement of the latest produced 80% solid load paste was due to a change made in the printing parameters, which led to an increase in the shear rates during the printing process and therefore a change in one of the test's parameters had to be changed in order to achieve more accurate results. This test measures the change in viscosity with time as the imposed shear rates are changed in three intervals, the first representing the rest state in the nozzle, the second simulating the printing step, and the third simulating the rest state after deposition is completed. The shear rate values have been explained previously in this report.

Figure 3.6 shows the results of the 3ITT test where the shear rate imposed in the second interval being 15 s^{-1} which is slightly higher than the calculated shear rate of 13.3 s^{-1} during the printing process, due to the print speed used for these pastes set to 2 mm/s . It should be noted that in all pastes analyzed, there is good recovery following the drop during the printing, a characteristic of pastes with thixotropic behavior, which is desirable for robocasting. Between both of Thomas's pastes, the paste with 82.5% solid load showed higher viscosity values at all steps, and an overall better curve when compared to the 84% solid load paste, which showed a slight increase in viscosity on the onset of the second interval of the test. For the 82.5% solid load that was reproduced at the start of this thesis work, the results show good thixotropic behavior, but due to its very high values of viscosity, the solid load was reduced to 80% solid load for future pastes. The paste with 80% solid load showed much better values of viscosity, although it was still considerably higher than Thomas's 82.5% solid load paste. Due to the high viscosity during the interval simulating the printing phase, it was decided to adjust the printing parameters, with the path width changed from 5 mm to 25 mm, and more importantly, the print speed was changed from 2 mm/s to 10 mm/s . Increasing the print speed meant that the shear rate during printing had to be recalculated, which led to a value of 66.7 s^{-1} . Therefore, following another test was undertaken for the 80% solid load paste, towards the end of the thesis work, where the shear rate in the second interval of the test was set at 70 s^{-1} .

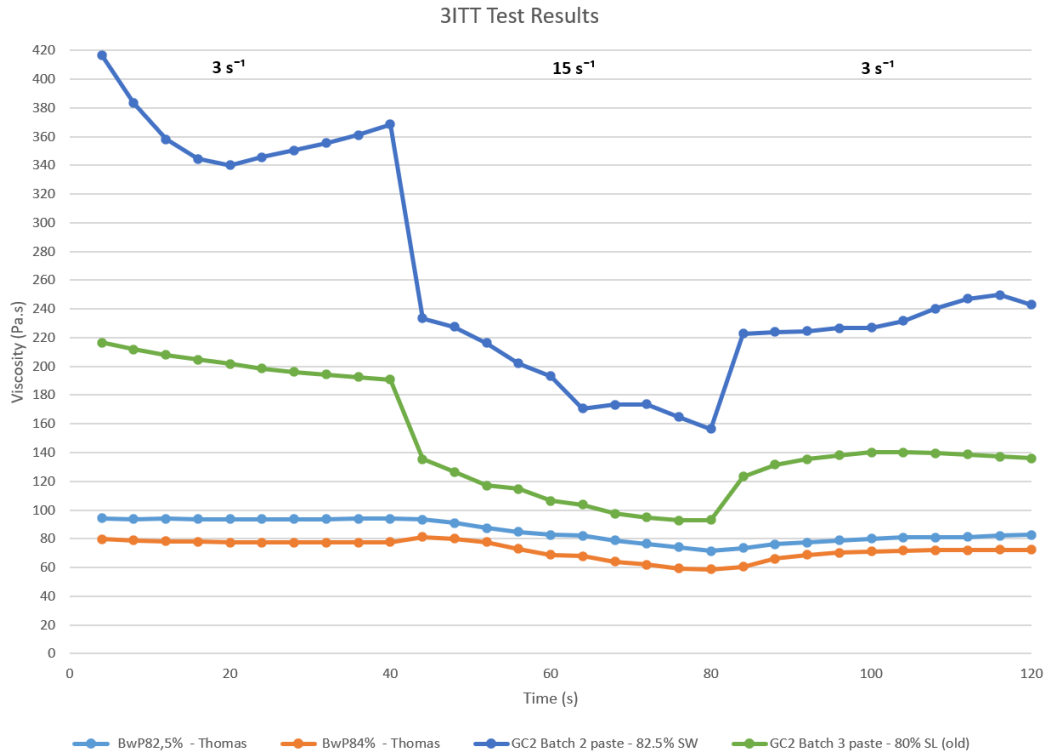


Figure 3.6: 3ITT results for pastes, where the second interval simulates printing condition with print speed of 2mm/s. Shear rates are written at the top of each interval.

Referring to the graph on Figure 3.7, it can be noted that the drop in viscosity in the second interval is more drastic, which is followed by good recovery of the viscosity at the rest state post-deposition. Furthermore, by comparing the values in viscosity between this paste and the 80% solid load one in the previous figure, it can be noted that the newer paste showed lower viscosity even at rest, which can be explained by both quality of the particle dispersion and test conditions as mentioned before. Another note of interest, is that the viscosity drops below all other pastes tested in the second interval, meaning that the higher print speed lead to an easier extrusion due to the reduction in viscosity. Therefore, it was determined that the change in printing parameters were more optimal for sample preparation.

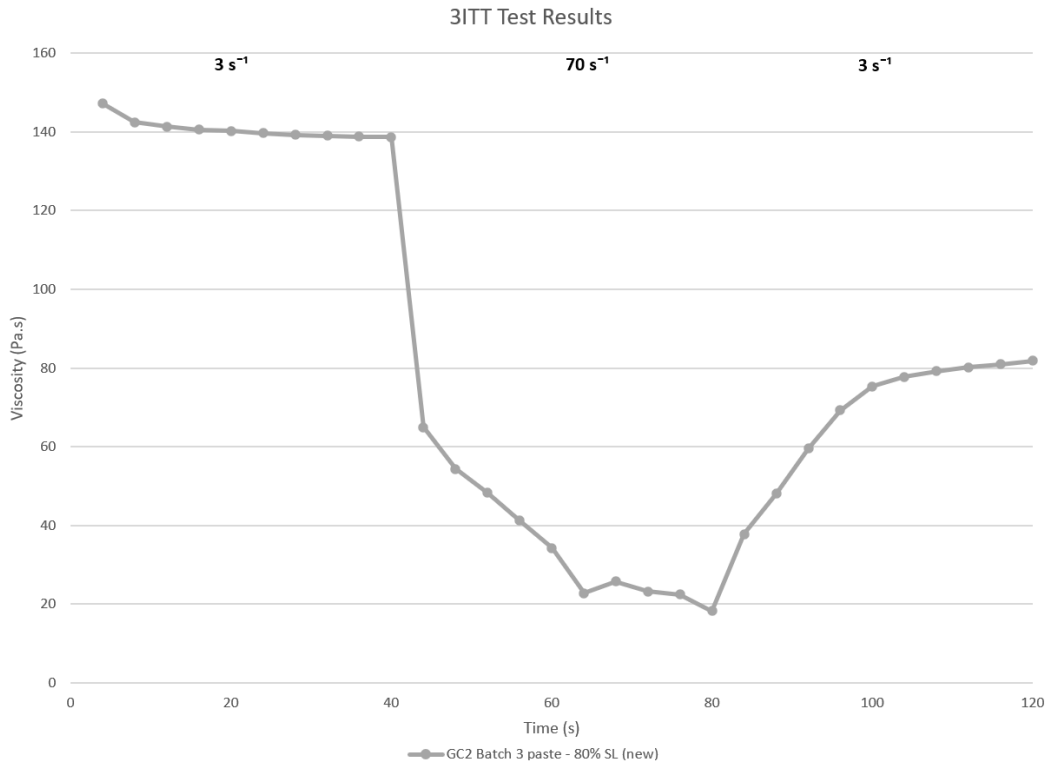


Figure 3.7: 3ITT results for 80% solid load paste produced later during the thesis work, where the second interval simulates printing condition with print speed of 10mm/s. Shear rates are written at the top of each interval.

3.3 Profilometer Test results

The profilometer was used on only one sample during the thesis work due to time constraints. Nevertheless, the sample tested provided useful insight in comparing the change in thickness before and after the joining process. Specifically, the sample tested was composed of a dual phase 70CGO-30STF82 OTM joined to a 20mm crofer disc, with the paste used for the joint consisting of 80% solid load GC2. Furthermore, the print speed used was 2mm/s and the path width was set to 5mm on Voxelizer 3.0. A measurement on only one side was performed due to the time constraint.

The results (see Figure 3.8) showed that after the drying step, the thickness of the printed profile was around $290\ \mu\text{m}$ and a width of around 2.5mm. Such values were expected given the set printing parameters, although due to the test having been done on one side, it cannot be assumed to be fully valid for all sections of the printed profile. Nevertheless, after the joining process, a reduction of the printed profile's thickness was observed, with the values for this specific sample found to be in the range of 137-186 μm in the analyzed section. It can be assumed that a similar reduction in the

profile thickness occurs in all other sections of the profile due to the application of the pressure during the joining process.

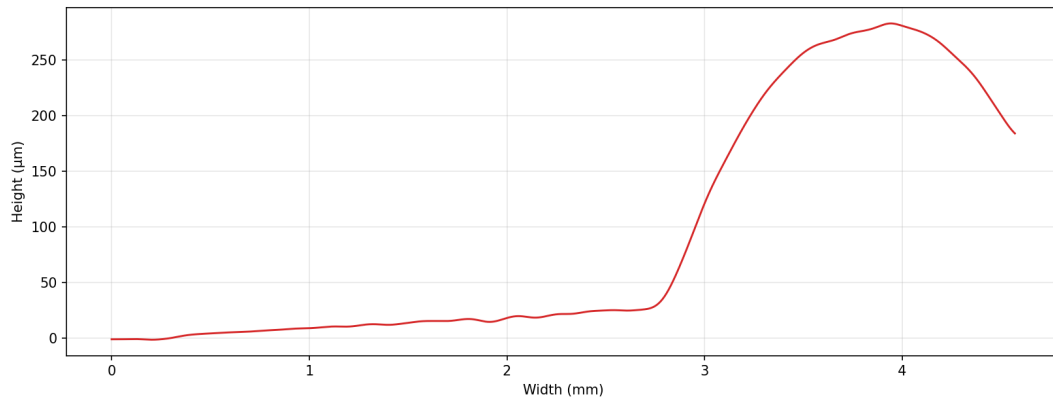


Figure 3.8: Measured printed profile by profilometer. Resulting curve has been smoothened.

For future work on this project, it is recommended that the profilometer be used more frequently in order to have a larger amount of results, with measurements performed on multiple sections of the printed profile recommended for having a more complete picture of the profile dimensions. Doing so would therefore lead to more accurate results, and would offer comparisons for profiles printed with different printing parameters, which would have offered further assistance in optimizing the deposition step.

3.4 TGA of GC2 Tape

For building the thermal treatment curve for a joining process that uses a tape casted joint, a TGA was performed on tape V3 with 67% GC2 solid load, which had been previously prepared by Thomas. The analysis was done on 8.30931mg of tape V3 at a rate of $10^{\circ}\text{C}/\text{min}$ in the temperature range of 35°C to 550°C , with this maximum temperature chosen to be below the glass transition temperature of GC2 glass. Figure 3.9 shows the TGA results in graph form with the derivative TGA curve, called derivative thermogravimetry (DTG), overlapped to show clearly the zones with the largest mass changes. On the left side of the graph the mass was normalized to show the total change of mass in percentage, with this axis belonging to the TGA results represented as a blue curve, while on the right side the first derivative curve in percentage belong to the DTG results represented as an orange curve. On the orange curve, excluding the noise present, peaks are used to determine the temperatures at

which the fastest rate of mass loss occur, which would then be used as dwell temperature points during the heating stage of the thermal treatment.

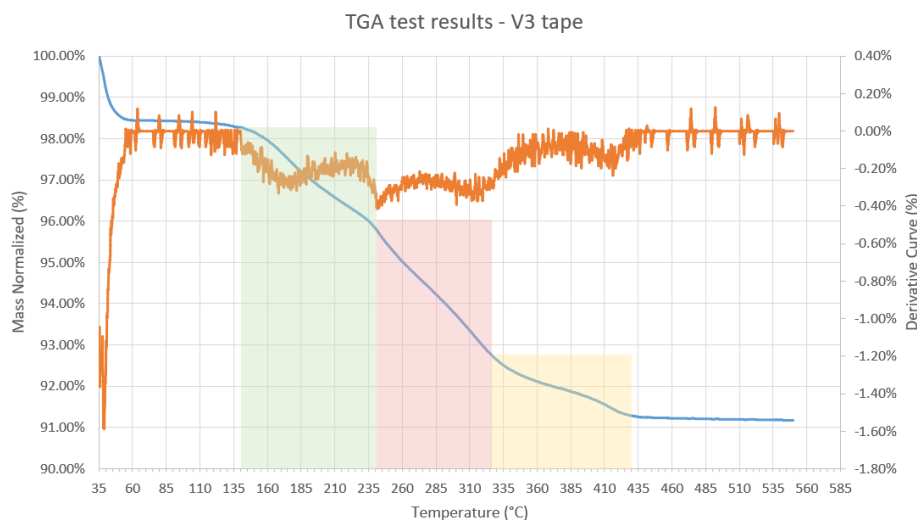


Figure 3.9: TGA and DTG curves superpositioned with zones of greatest mass changes highlighted

The total mass loss was found to be 8.84%, with the mass losses happening in stages. Initially, there is a high slope signifying a high rate of mass loss in the range below 55 °C which could be due to residual ethanol that was present in the tape or due to the evaporation of water vapor that could have accumulated during the tape storage period. Highlighted in green is the first zone of interest, where the DTG curve shows the presence of two peaks with one being at around 170 °C and another at 240 °C with the latter peak present at the intersection of the green and red zones of interest. In the red highlighted zone, another peak is present at 320 °C, and in the yellow zone another peak is at around 420 °C. These peaks lie in the ranges of degradation of the additives present in the tape formulation such as terpineol, disperbyk-103, PEG-400 and PVB.

Due to the failure in reproducing new usable tape in this thesis work, no further TGA tests were undertaken. It is recommended that for every tape successfully produced to be tested by TGA in order to further optimize the the thermal treatment for the tape casted joint.

3.5 Tape formulation attempted changes

Following the creation of a thermal treatment curve specific to tape casted joints, the goal was to recreate the tape. Due to time constraints, and the priority given

to robocasting, only two attempts were made throughout the thesis work to use tape casting.

The first attempted change involved replacing ethanol with butanol while keeping the solid load at 67% (see Table 2.5), where the idea that butanol is more stable than ethanol and would therefore evaporate slower during the ink preparation step. Furthermore, a slower drying step could perhaps lead to a lower chance of cracks forming in the tape, which has a higher chance of occurring with faster drying such as when ethanol is used. Using the tape caster, the doctor blades were set at a height of $400\text{ }\mu\text{m}$ before spreading the slurry on the silicon coated mylar. Overall, it took 4 days for the tape to fully dry, although the edges of the tape remained lightly wet. Due to the longer period of drying, which took place under a fume hood, some contaminant particles accumulated on the surface of the tape. In addition to this issue, the tape remained stuck to the silicon coated mylar, possibly due to the fact that after drying the tape's thickness reduces even more than the thickness imposed by the doctor blades, which was already too thin. As a result, this tape was discarded. Figure 3.10 shows the tape during its drying step.



Figure 3.10: Tape during drying step

The second attempted change involved going back to the original formulation with ethanol, but the solid load was increased to 71%. In this case, the idea was that an increase in the solid load would lead to a lower shrinkage of the tape thickness post-drying. Using the tape caster, the height of the doctor blades were set to $550\text{ }\mu\text{m}$

this time. Unfortunately, the same issue with the tape remaining stuck to the silicon coated mylar persisted. Minor contaminant accumulation on the surface occurred too, but less than before probably due to a cleaner working area under the fume hood during the tape's drying period. Furthermore, when the mylar with the dried tape was moved around, some cracks formed leading to some parts of the tape breaking apart. Therefore, this tape was also discarded.

3.6 Sample Test results

Throughout the thesis work, 17 samples were prepared. Out of these sample, 4 broke following the thermal treatment, and 3 were sent to RSE for leakage and thermal aging tests. As mentioned previously in this report, the samples consisted of three parts, the OTM, the glass-ceramic sealant, and the metal support. Two main OTMs were used, the single-phase LSCF and dual-phase 70CGO-30STF82, which were thin ceramic discs with a diameter of around 18.5-19.5mm. For the metal supports, both Inconel 625 and Crofer 22 APU were used, with smaller samples using circular metal samples of 20mm diameter and larger samples, such as those sent to RSE, using the ones with 40mm diameter. Inconel 625 was mainly used in tandem with LSCF membranes due to their CTE compatibility, although there was an attempt to join it with the dual phase membrane. Crofer 22 APU, on the other hand, was used only with dual-phase 70CGO-30STF82 membranes, also due to their CTE compatibility.

In order to verify the quality of the joints, two tests were done to check the microstructure of the glass-ceramic sealant. These tests were the X-ray computed tomography (CT) scan, and the scanning electron microscopy (SEM) test, where their focus was in detecting defects such as cracks and pores. By detecting these defects, improvements in the joining processes were made in the following samples prepared in order to minimize the growth of such defects, as they could cause failure during operating conditions if not controlled. CT scans were not done to all samples, but they were crucial in the case of the three sample sent to RSE as they required the detection of defects without destructive testing. For all other samples that were successfully joined, SEM tests were performed, which provided useful insights on the quality of the sealants.

In this thesis work, most samples prepared utilized 20mm circular metal supports, with the exception of four samples that utilized 40mm metal supports, out of which three were sent to RSE and one was tested using both CT scanning and SEM. Robocasting was the primary method used to deposit the GC2 paste for the glass-ceramic

sealant, with the exception of 2 samples that used a previously tape casted tape (V3 by Thomas) as the joint.

3.6.1 CT Scan Test results

Throughout the thesis work, 7 samples out of the 17 prepared were tested with the CT-scan X-Ray machine. These results helped verify whether any cracks detected by the SEM were due to the joining process or the cutting and polishing process that took place during the sample preparation steps preceding the SEM test. For the samples sent to RSE, the CT scan served as the only method to test the joint due to the test's non-destructive nature.

LSCF joined to Inconel 625

Before the decision to start using the CT scan, a previously prepared sample of LSCF joined to Inconel 625 via a glass-ceramic joint made by an 82.5% solid load paste was made. As mentioned before in this report, the thermal treatment for robocasted joints had been adjusted based on Thomas's thermal treatment curve, with the change done to the heating step in which the heating rate was reduced to $0.5^{\circ}\text{C}/\text{min}$, and weights of around 73g were added on top on the membrane to induce a pressure for the joining process to be effective. Following that sample's test by SEM, cracks were detected with minor porosity (and improvement from Thomas's final samples). Due to the sample preparation steps preceding the SEM (mentioned previously in this report), it was decided to perform CT scans on future samples, when the time allowed, before doing SEM analyses. Since for the SEM analysis the cutting involved only one section in the sample, which did not offer a complete picture of the quality of the joint in all sections of the sample, the CT scan offered the chance to see whether any other defects could be present at all sections of the joint. Furthermore, due to the polishing and cutting steps before SEM analysis, there was a chance that cracks could have been induced by them, so the CT scan offered a chance to compare their results with the SEM analysis results.

Only one sample of LSCF joined to Inconel 625 was tested by the CT scan during this thesis, as the focus was shifted later from LSCF membranes to the new dual phase membranes. It should be noted that the deposited profile is uneven due to multiple reasons. Firstly, inaccurate centering of the sample on the platform of the Zmorph 3D machine used for robocasting was an issue present due to the manual nature of sample positioning pre-printing, which over time was partially solved by having a more accurate measurement of the dimensions on the platform and setting the origin on

a more convenient point. Secondly, in the case of this sample, the paste used for robocasting had an 82.5% solid loading, and due to its high viscosity, uneven printing occurred, which is evident by the printed profile. Another issue that is particular to this sample, was that the weights were not fully centered on top of the membrane during the thermal treatment, leading to an over loaded side and an under loaded side. As a result, the unloaded side of the glass-ceramic was not fully in contact with the LSCF membrane. Figure 3.11 showed the view from above of the glass-ceramic layer in contact with the LSCF membrane, with the uneven profile visible, and areas with weak adhesion to the membrane notable. Additionally, a small amount of glass-ceramic is present close to the center due to the initial wrong positioning of the sample on Zmorph 3D's platform during ink deposition, which was quickly corrected, but was left to help differentiate the sample from another sample that was being prepared at the same time.

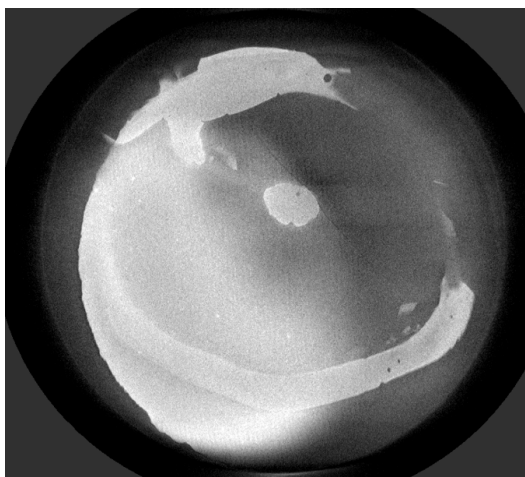


Figure 3.11: Top view of CT scanned LSCF - GC2 82.5% SL - Inconel 625, at glass-ceramic interface with membrane.

70CGO-30STF82 joined to Crofer 22 APU

Due to previous failed attempts to join the dual phase membrane, 70CGO-30STF82, to Inconel 625, with this failure attributed mainly to CTE mismatch, all dual phase membranes that were tested were joined to Crofer 22 APU.

For the first sample tested of this composition, an 82.5% solid load GC2 paste was used and deposited by robocasting to make the glass-ceramic joint, with the thermal treatment being accelerated due to time limitations (see the thermal treatment curve on Figure 2.19 with a cooling rate of $0.7^{\circ}\text{C}/\text{min}$) Due to issues mentioned previously, the printing profile was uneven. Unlike the sample with LSCF joined to Inconel 625, the profile seemed smoother overall, with the exception of a few pores that can be

noted in Figure 3.12. This smoothness in the profile, which is further verified by the sample's SEM analysis, can be attributed to a higher CTE compatibility between the dual phase membrane and Crofer 22 APU. However, two main issues were present that were changed for the following samples. For this sample, the membrane was placed on the glass-ceramic with its porous surface facing it, as the dense layer had not been identified and marked beforehand. Furthermore, the Crofer 22 APU did not undergo a pre-oxidation step before joining.

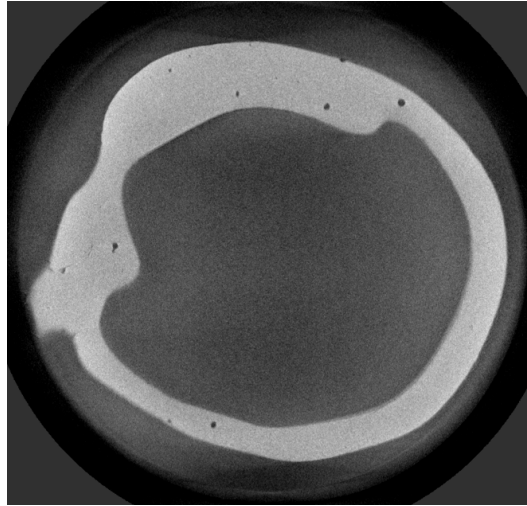


Figure 3.12: Top view of CT scanned 70CGO-30STF82 - GC2 82.5% SL - Crofer 22 APU, in the mid-section of the glass-ceramic layer.

In the following sample tested, which was composed of the same membrane and metal, the Crofer 22 APU had been pre-oxidized previously and for the paste used for robocasting, the formulation was changed to an 80% solid load and the thermal treatment was the same as one for the previously tested sample. Additionally, the membrane had its dense side previously marked which helped in placing the membrane correctly on the printed profile. Due to the reduction in the paste's viscosity, the printed profile was closer to an annular shape than previous samples, albeit with some unevenness at the point where the printing started due to reasons mentioned previously (see Figure 3.13). Some porosity was detected and no cracks were detected with this test. It should be noted that due to the resolution of this test, it is not definitive to say that no cracks are present, which is why an SEM analysis is always required after a CT scan. A critical issue that remained was the incorrect manual centering of the weights, which led to an uneven weight distribution on the glass-ceramic layer leading to sections staying completely unconnected to the membrane, as seen on Figure 3.14. More samples of the previous sample's configuration were produced, but due to time limitations, only the SEM analysis was performed.

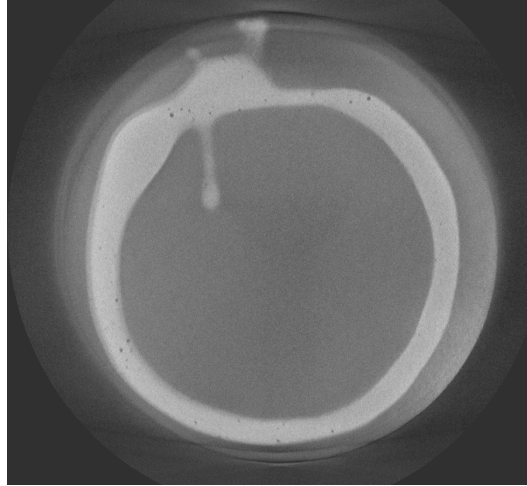


Figure 3.13: Top view of CT scanned 70CGO-30STF82 - GC2 80% SL - pre-oxidized Crofer 22 APU, in the mid-section of the glass-ceramic layer.

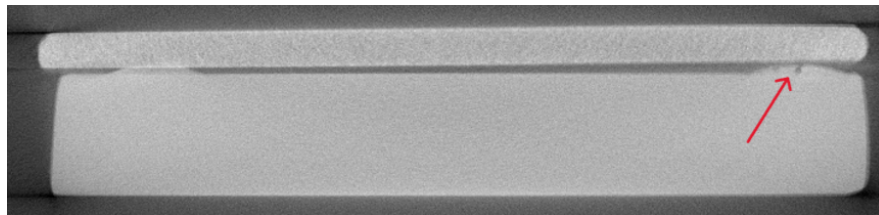


Figure 3.14: Side view of CT scanned 70CGO-30STF82 - GC2 80% SL - pre-oxidized Crofer 22 APU. Side with a pore and poor adhesion of glass-ceramic to membrane is pointed at with an arrow

The final sample tested by the CT scan was made in order to simulate the samples sent to RSE, with the goal to do an SEM test on the sample in order to characterize the joint's microstructure. Figure shows the CT scan results of the sample. Overall the results were comparable to that of the samples for RSE, with no cracks detected in the joint, and minor porosity.

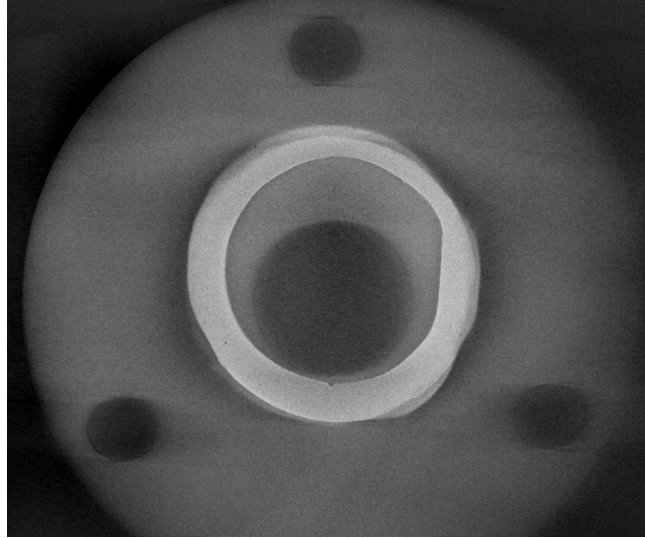


Figure 3.15: Top view of CT scanned 70CGO-30STF82 - GC2 80% SL - pre-oxidized Crofer 22 APU, in the mid-section of the glass-ceramic layer.

Samples sent to RSE

For the three samples prepared for RSE, the only tests that were done on them before shipping to RSE S.p.A., was the CT scan test, due to its non-destructive nature. All three samples consisted of a 40mm pre-oxidized Crofer 22 APU disc with a hole in the middle, joined to the dual phase membrane by a glass-ceramic sealant that was created via robocasting using a GC2 paste with a solid load of 80%, with the thermal treatment reverted to the initial change made in which the cooling rate was $0.5^{\circ}\text{C}/\text{min}$ (see Figure 2.18). Changing the thermal treatment was needed due to crack formation being prone to the cooling step, with a slower cooling having a lower chance of cracks occurring. Furthermore, the printing parameters were changed compared to the previously tested samples, as mentioned previously in the report (see Figure 2.10).

For all three samples, the glass-ceramic sealant showed good adhesion to both adjacent surfaces, with some porosity present and minor cracks detected. Due to changes made to the printing parameters, and care that was taken in centering the samples on the platform belonging to the Zmorph 3D machine for robocasting, the resulting printed profiles had the desired annular shapes. Furthermore, correct placement of the weights on top of the membranes led to a good distribution of the pressure on the printed profile, which helped improve the adhesion of the glass-ceramic to both metal and membrane. Using the CT scan's software, the dimensions of the joints were measured to check both thickness and width of the glass-ceramic joints. All sections measured for the three samples showed desirable dimensions for the thickness, in which the dimensions ranged from around 150 to $259\mu\text{m}$, with differences from side to side

attributed to the pressure distribution on the joint during the joining process. For the width of the joints, the dimensions are considered acceptable, with dimensions ranging from 2.7 to 3.7mm, although future changes in the printing parameters can help in ensuring that the width stays below 3mm. Particularly, the path width parameter on Voxelizer 3.0, which dictates the volume of material extruded, can be adjusted in the future. Below, the figures for the three RSE samples are present, with their names differentiated by their numbering (from 1 to 3).

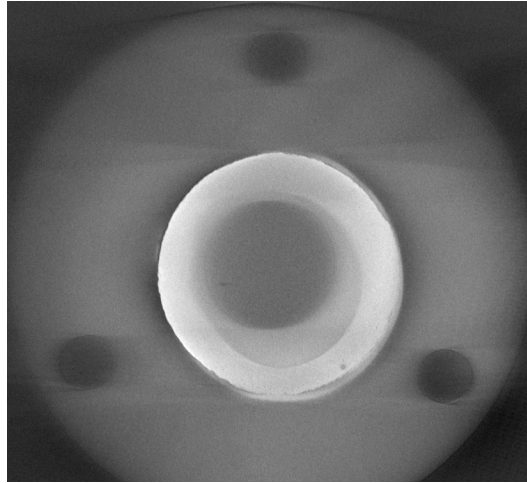


Figure 3.16: Top view of CT scanned RSE sample 1 (70CGO-30STF82 - GC2 80% SL - pre-oxidized Crofer 22 APU), at the glass-ceramic interface with membrane.

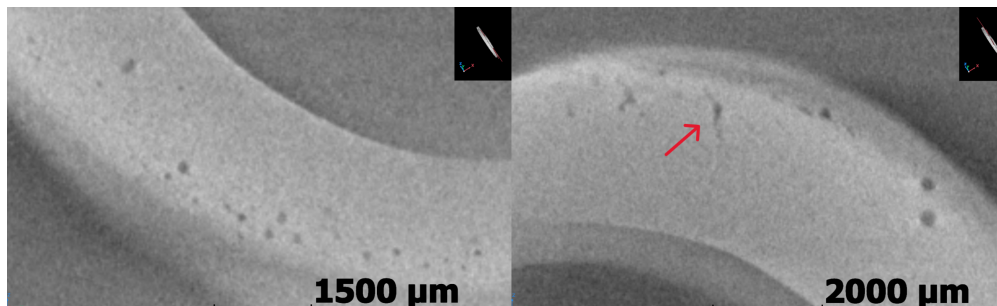


Figure 3.17: Closeup top view of CT scanned RSE sample 1, in the mid-section of the glass-ceramic layer. Some porosity can be seen. Furthermore, a crack is present (see red arrow).

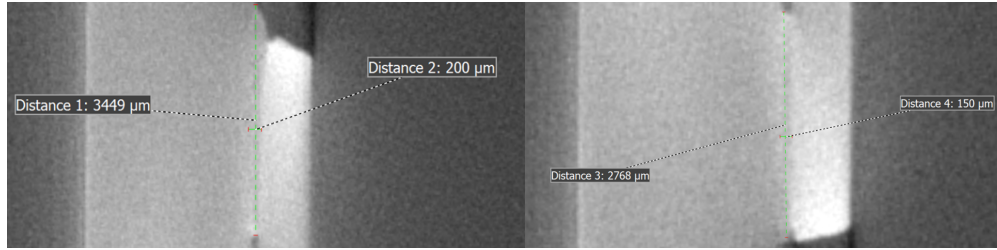


Figure 3.18: Closeup side view of CT scanned RSE sample 1. Distances 1 and 3 are the width of the joint, and distances 2 and 4 are the thickness.

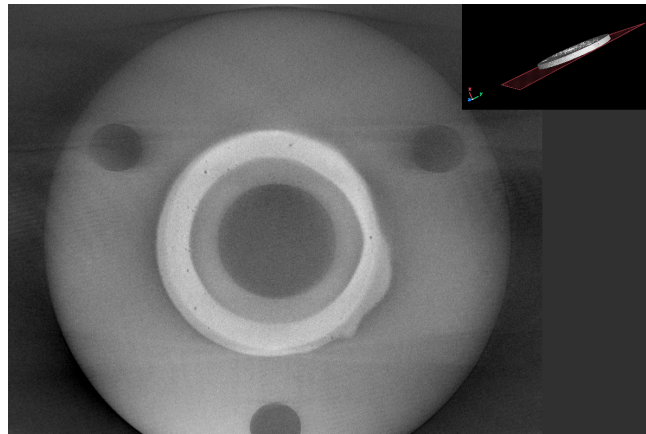


Figure 3.19: Top view of CT scanned RSE sample 2 (70CGO-30STF82 - GC2 80% SL - pre-oxidized Crofer 22 APU), in the mid-section of the glass-ceramic layer.

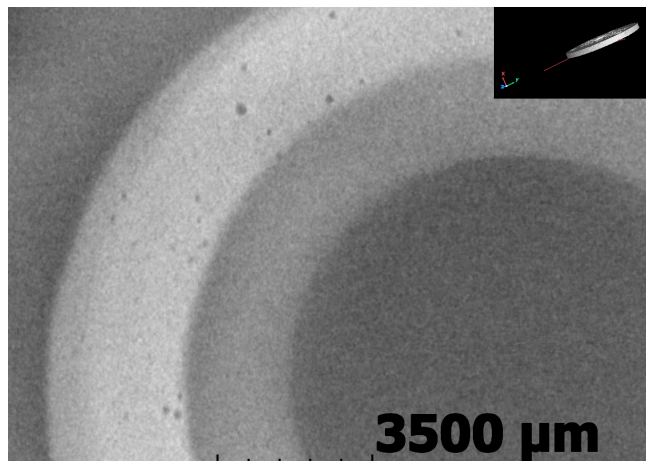


Figure 3.20: Closeup top view of CT scanned RSE sample 2, in the mid-section of the glass-ceramic layer. Some porosity can be seen, and no cracks were detected.

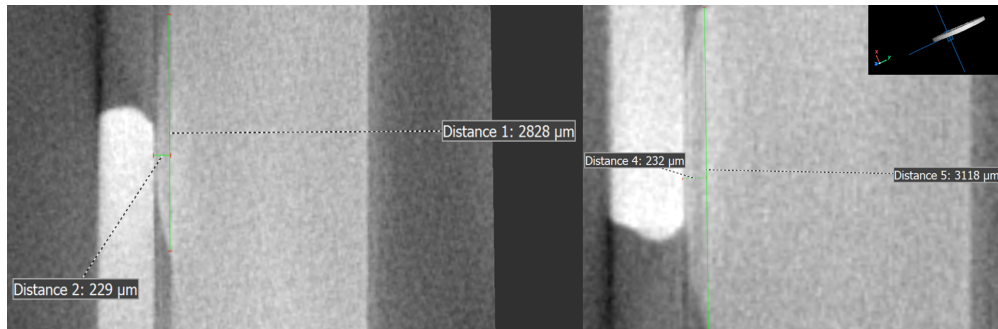


Figure 3.21: Closeup side view of CT scanned RSE sample 2. Distances 1 and 5 are the width of the joint, and distances 2 and 4 are the thickness.

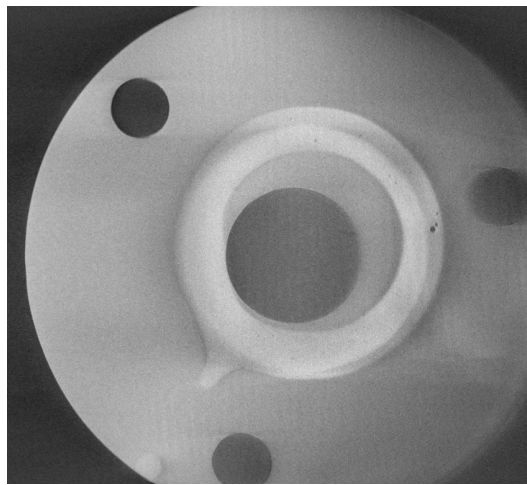


Figure 3.22: Top view of CT scanned RSE sample 3 (70CGO-30STF82 - GC2 80% SL - pre-oxidized Crofer 22 APU), at the glass-ceramic interface with the metal.

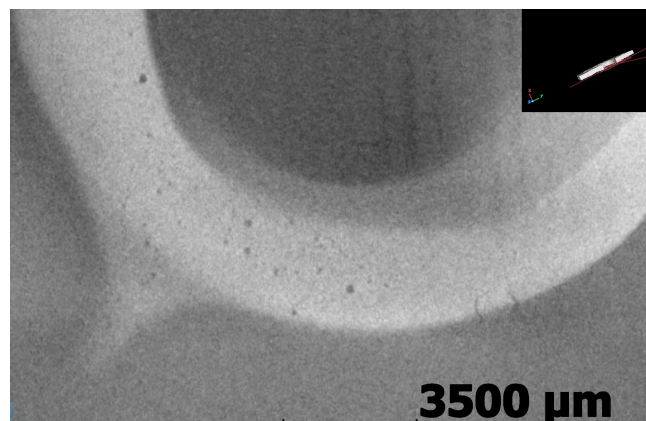


Figure 3.23: Closeup top view of CT scanned RSE sample 3, in the mid-section of the glass-ceramic layer. Some porosity can be seen, and minor cracks were detected (not marked).

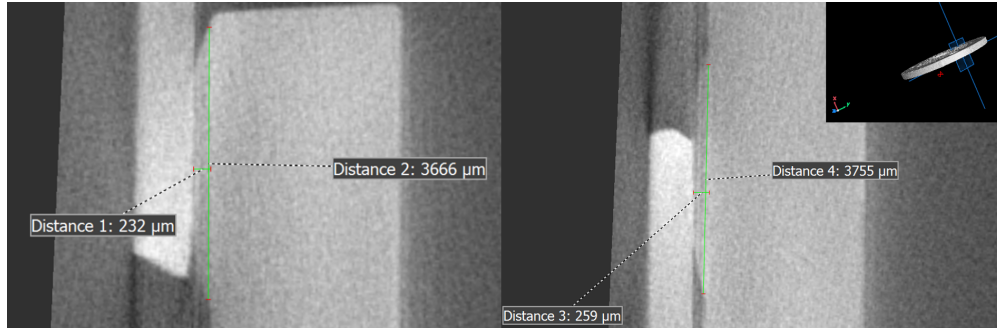


Figure 3.24: Closeup side view of CT scanned RSE sample 3. Distances 1 and 3 are the width of the joint, and distances 2 and 4 are the thickness.

Following the CT scanning of these three samples, they were packaged and sent to RSE S.p.A. for leakage testing and thermal aging.

3.6.2 SEM Test results

Throughout this thesis work, 10 samples were analyzed via the SEM out of the 17 samples prepared. SEM was the most important step in sample testing, due to its ability in detecting pores and cracks at the microstructure scale with a high resolution. It should be noted that none of the samples prepared for RSE were tested via the SEM, but a final sample with the same properties and components was prepared in order to have a reference to compare to them. Some of these tests are reported and discussed in the following sections.

LSCF joined to Inconel 625

The first sample of LSCF joined to Inconel 625, used 82.5% solid load for the robocasting paste's formulation. For the thermal treatment, the one used was the one on Figure 2.18. Following the SEM analysis (see Figure 3.25), good adhesion of the glass-ceramic to both metal and membrane was detected, although large cracks were detected, which was attributed to a potential CTE mismatch between the membrane and metals. Porosity seemed reduced when compared to older joints made by Thomas, with this improvement attributed to the slower heating rate in the thermal treatment. Another aspect that can be noted is that due to the manual placement of the weights on top of the membrane, it was difficult to keep it centered accurately, and therefore one side of the joint was not very effective due to the pressure being unevenly distributed. Furthermore, due to the nature of the crack formation in this sample, it was decided for the following samples to do a CT scan analysis before proceeding with the SEM analysis.

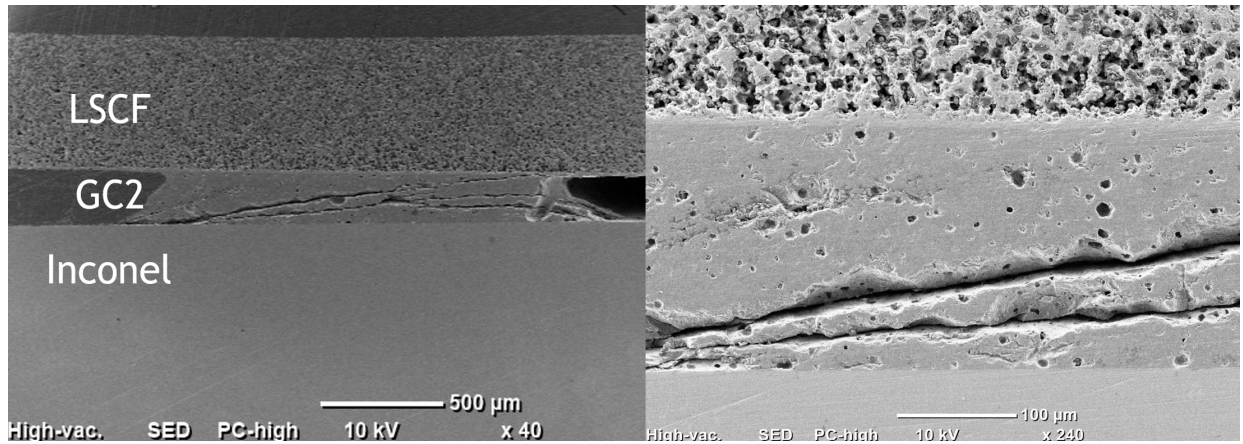


Figure 3.25: SEM images of one side of the joint in the sample LSCF - GC2 82.5% SL - Inconel 625, with a closeup view on the right. Width of this side of the joint was measured to be around 2mm, and thickness around 206 μm .

In the case of the following samples composed of LSCF and Inconel 625, the cooling rate was slightly accelerated due to time constraints in the lab, with the thermal treatment followed seen on Figure 2.19. For the following sample of LSCF joined to Inconel 625 (for which its CT scan results were analyzed previously in this report), the results showed low porosity like the first sample, although the cracks were more drastic (see Figure 3.26). The main reason was due to the inaccurate placement or shift of the weights above the membrane during the joining process, which overloaded one side of the joint.

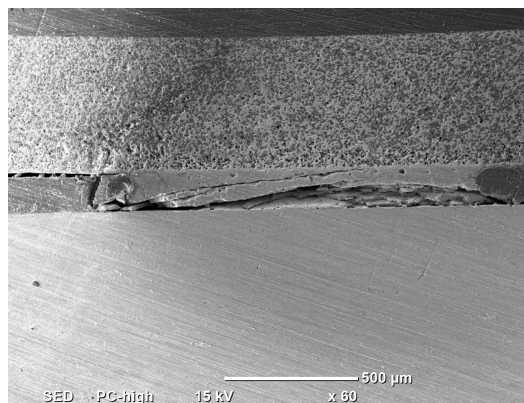


Figure 3.26: SEM image of one side of the joint in the sample LSCF - GC2 82.5% SL - Inconel 625 (2nd attempt). Width of this side of the joint was measured to be around 1.55mm, and thickness around 134 μm , noting that this side was overloaded during the joining process.

Another sample was prepared with 80% solid load for the robocasting paste, instead of the previously used 82.5% solid load, but following the thermal treatment, it came out broken. Due to the consistent formation of cracks in the joint between LSCF and Inconel 625, it was decided for the rest of the thesis work to focus exclusively on joining the dual phase membrane to Crofer 22 APU. This consistent formation of cracks were attributed to CTE mismatch between LSCF and Inconel 625, which due to their different expansion rates stressed the glass-ceramic layer causing the cracks to form.

70CGO-30STF82 joined to Crofer 22 APU

Before attempting to join the dual phase membrane to Crofer 22 APU, an initial attempt used Inconel 625, with the robocasting paste used having an 82.5% solid load. Following the thermal treatment step (see Figure 2.18), the sample came out broken. Therefore, it was decided for samples utilizing the dual phase OTM to use Crofer 22 APU for the metal. As mentioned previously, due to laboratory time constraints, the cooling rate was slightly accelerated, with the thermal treatment used being the one on Figure 2.19. This thermal treatment was reverted to the initial one for the samples prepared for RSE and also for the last sample prepared (to simulate the RSE samples for SEM analysis).

The first sample that was made joining the dual phase OTM to Crofer 22 APU (without pre-oxidation) used a robocasting paste with 82.5% solid load, and following the thermal treatment it was successfully joined due to the higher CTE compatibility between membrane and metal. Following the SEM analysis (see Figure 3.27), no cracks were detected in the joints, and in terms of porosity, a very minimal amount of pores were detected. However, due to the membrane's dense side not being previously marked, the joining occurred with the porous side instead. This was corrected in the following samples as a newer batch of dual phase OTMs were sent to the lab by RSE S.p.A. with the dense side marked. Furthermore, due to issues mentioned with the paste previously, the following samples utilized a robocasting paste with an 80% solid load. Other samples of this configuration utilized pre-oxidized Crofer 22 APU, in order to ensure better joining properties and to avoid any chromium evaporation into the glass-ceramic joint, which would cause failure during thermal aging.

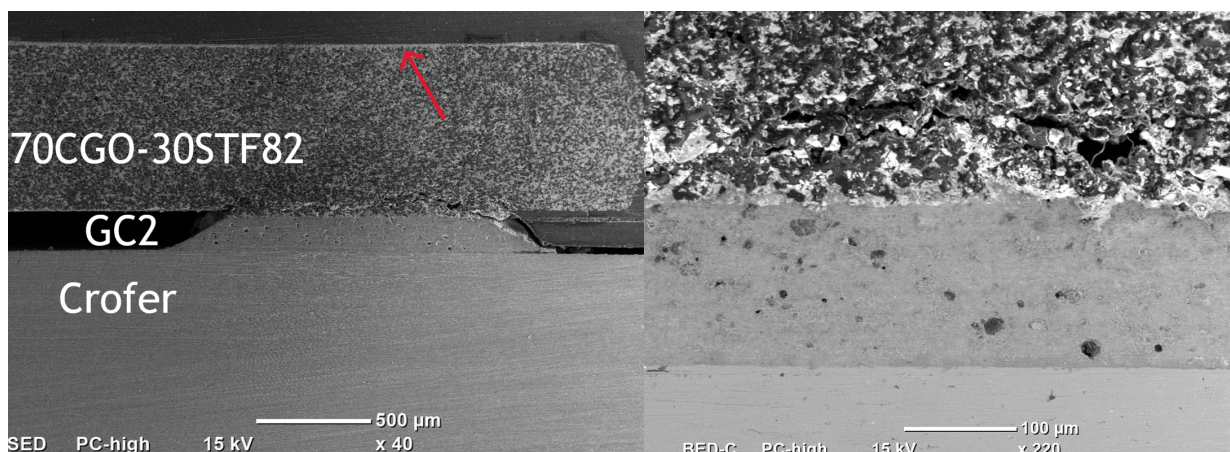


Figure 3.27: SEM images of one side of the joint in the sample 70CGO-30STF82 - GC2 82.5% SL - Crofer 22 APU, with a closeup view on the right. Width of this side of the joint was measured to be around 1.56mm, and thickness around 144 μm . Note the dense side (see red arrow) of the membrane.

Another joined sample with dual phase OTM and Crofer 22 APU was prepared, with the new paste formulation adjustment. Compared to the previous sample mentioned, the porosity was more prevalent, and a crack was detected in the joint section (see Figure 3.28). An explanation for the increase in porosity compared to the previous sample can be that due to the joint that was previously done on the porous layer, more pathways for gases to escape via the pores of the OTM were present. In terms of the crack, the cooling rate of the accelerated thermal treatment can be considered a possible culprit. As a result of this crack formation, the samples prepared for RSE used the initial thermal treatment curve in order to ensure a better quality joint with less to no crack formation (as further confirmed by their CT scan results).

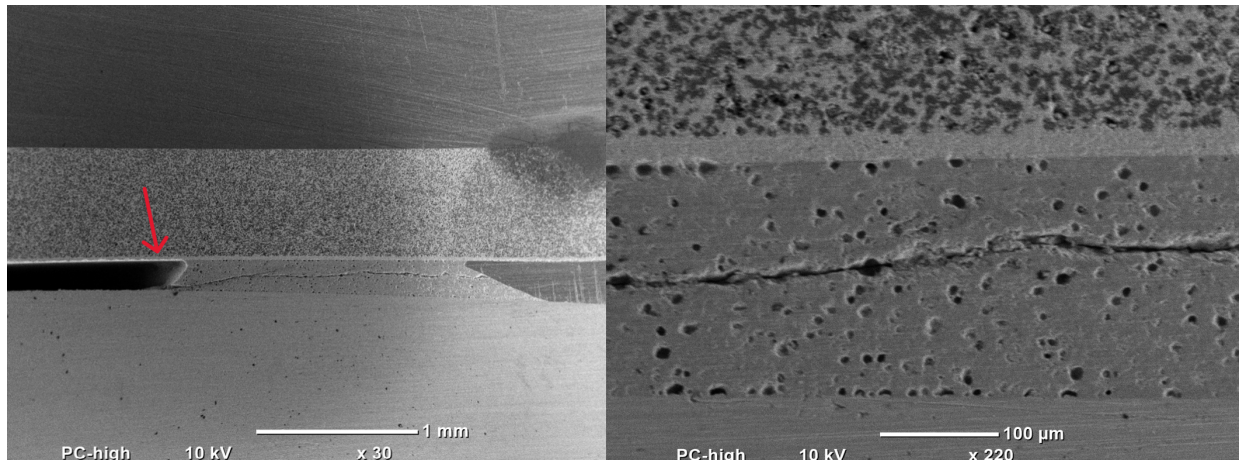


Figure 3.28: SEM images of one side of the joint in the sample 70CGO-30STF82 - GC2 80% SL - pre-oxidized Crofer 22 APU, with a closeup view on the right. Width of this side of the joint was measured to be around 2.32mm, and thickness around 183 μm . Note the dense side (see red arrow) of the membrane.

Another sample was prepared following the preparation of the three sample intended for RSE S.p.A., with the same properties. Figure 3.29 shows that there were no crack formations, with low porosity present and good adhesion of the glass-ceramic to the adjacent materials. Furthermore, no crack formations present can be attributed to the use of the thermal treatment (see Figure 2.18), as cracks typically form during the cooling rate, which in this case was carefully controlled.

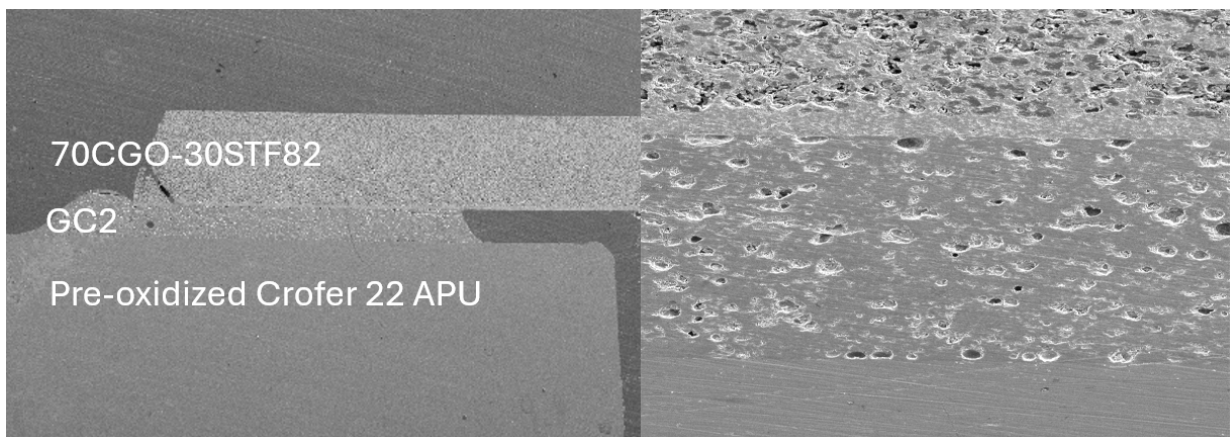


Figure 3.29: SEM images of one side of the joint in the sample 70CGO-30STF82 - GC2 80% SL - pre-oxidized Crofer 22 APU, with a closeup view on the left. Width of this side of the joint was measured to be around 3.3mm, and thickness around 232 μm .

Tape casted joint

For this thesis work, only one attempt was made to join OTM to metal via a tape casted joint, where in this case utilized a previously prepared tape by Thomas, which was made with a slurry with a 67% solid load. Following a TGA analysis, a thermal treatment curve was built for tape casted joints (see Figure 2.20), with the cooling rate accelerated due to laboratory time constraints at the time. Two samples were prepared simultaneously, one that used LSCF and Inconel 625, and the other used the dual phase OTM and Inconel 625. Due to CTE mismatch between the dual phase membrane and Inconel 625, the sample came out broken following the end of the thermal treatment.

In the case of the sample with LSCF, the same came out joined. The SEM analysis (see Figure 3.30) showed, in the section tested, that the glass-ceramic layer was almost completely detached from the metal. Adhesion was better with the LSCF dense side, although a concentration of pores were detected at the interface. A probable cause for these could be that the cooling rate was too fast and would need to be reduced from $0.8^{\circ}\text{C}/\text{min}$ to $0.5^{\circ}\text{C}/\text{min}$. The thermal treatment curve can also require further adjustments if future tapes were made and analyzed via TGA.

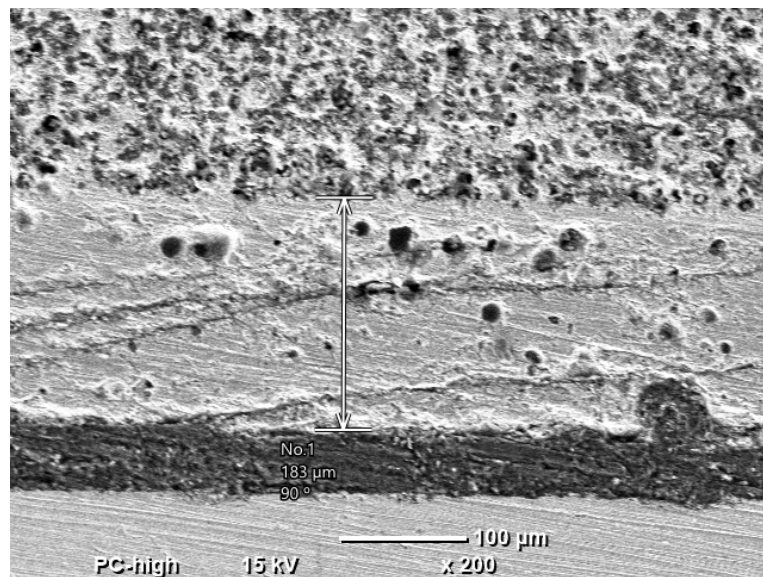


Figure 3.30: Cross-sectional view by SEM of LSCF-V3 tape-Inconel 625 sample. Thickness of the glass-ceramic layer is noted to be $183\ \mu\text{m}$.

4 Conclusion

This thesis focused on the development and optimization of a glass-ceramic sealant, based on GC2 glass, and its deposition techniques for the joining of Oxygen Transport Membranes to metal supports, building on the previous work carried out at Politecnico di Torino in collaboration with RSE S.p.A. The goal was to further improve the robocasting paste formulation and printing parameters, to develop a more effective thermal treatment curve, and to explore tape casting as a complementary deposition technique. In addition to the LSCF single-phase membranes and Inconel 625 metal supports studied in previous work, this thesis introduced a newly developed dual-phase membrane, 70CGO-30STF82, together with Crofer 22 APU metal supports, as potential alternatives.

The work progressed by first preparing and characterizing six batches of GC2 glass, verifying their particle size distribution and thermal properties through DSC testing. For robocasting, the paste formulation was adjusted by reducing the solid load from 82.5% to 80%, which together with an increase in the print speed from 2 mm/s to 10 mm/s, improved the paste's shear-thinning and thixotropic behavior, as confirmed through flow sweep and 3ITT testing. This translated into more even, annular printed profiles and better extrudability during deposition. In parallel, the thermal treatment curve used during the joining process was refined, with the heating rate reduced to $0.5^{\circ}\text{C}/\text{min}$ initially in the work and the cooling rate eventually reverted to a slower $0.5^{\circ}\text{C}/\text{min}$ for the final samples, as this was found to reduce the formation of cracks compared to the faster cooling rates used earlier in the work. Tape casting was also attempted as an alternative deposition method, where a TGA analysis was used to design a dedicated thermal treatment curve, although this technique ultimately did not yield a usable tape due to persistent adhesion issues with the casting substrate.

Throughout the thesis work, seventeen samples were prepared, with three of them sent to RSE for leakage and thermal aging testing. Early samples that were prepared suffered from porosity and occasional cracking, largely linked to inconsistencies in the manual placement of the weights used during joining, as well as to CTE mismatches, particularly between LSCF and Inconel 625. Focus was diverted, following the continu-

ous ineffective joints between LSCF and Inconel 625, to the new dual phase membrane and Crofer 22 APU, where both had better CTE compatibility. Furthermore, following the changes applied to the printing parameters and thermal treatment, both porosity and crack formation were noticeably reduced. This was confirmed by CT scanning of the samples prepared for RSE, none of which showed any notable cracks, and which exhibited lower porosity than earlier samples, representing a noticeable improvement over the course of the thesis. Tape casting, on the other hand, remained an open problem, with both attempted formulation changes failing to produce a tape that did not stick to the mylar or crack during handling.

Overall, robocasting was confirmed as a reliable and promising deposition technique for the GC2 glass-ceramic sealant, and the work carried out throughout the thesis lead to an improvement in both the paste formulation and the joining process compared to previous works. Results showed that LSCF and Inconel 625 joined by a glass-ceramic sealant based on GC2 were incompatible due to CTE mismatch and therefore, focus on them was discontinued. Future work should prioritize the dual-phase 70CGO-30STF82 membrane joined to pre-oxidized Crofer 22 APU, or another metal with comparable properties, given the promising results observed. That said, residual porosity and occasional cracking remain unresolved challenges that will need further attention before the process can be considered fully mature. For future work, it is recommended that profilometer analysis be used more systematically and on a larger number of samples, in order to better characterize the deposited paste profile across different printing parameters. Further adjustments to the printing parameters could also be recommended to reduce the width of the printed profiles, and to also decrease amount of paste needed for each deposition. The diameter of the printed profile can also be reduced from 18mm to a range of 15 to 16mm in order to ensure that all the deposited paste remains within the diameter of the membranes. Designing dedicated sample holders to assist with the weight placement step would likely help reduce the inconsistencies observed in this thesis, and could be a potential solution to avoid pressure disequilibrium on the printed profile, which could potentially lead to reduced crack formation. Furthermore, tape casting can still be investigated further as another deposition method in order to reproduce usable tapes, with a potential adjustment in the tape formulation recommended as a possible solution, with future TGA testing of each newly produced tape recommended for further refinement of the thermal treatment curve for tape casted joints.

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