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Authors(s)	Breen, Aidan, Twomey, Barry, Byrne, Greg, Dowling, Denis P.
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Comparison between microwave and microwave plasma sintering of nickel powders

A. Breen, G. Byrne, B. Twomey and D. P. Dowling

School of Electrical, Electronic and Mechanical Engineering,

University College Dublin, Belfield, Dublin 4, Ireland

Abstract

There is considerable interest in processing technologies which can lead to more energy efficient sintering of metal powders. The use of microwave sintering in particular leads to reduced energy usage during sintering as the volumetric heating process is considerably more efficient compared with resistance heating. In this study the use of a novel plasma microwave processing technology for the sintering of nickel powder discs is evaluated. The sintering study was carried out on 20 mm diameter by 2 mm thick pressed discs of nickel powder, with mean particle size of 1 µm. The discs were fired in a 5 cm diameter microwave (2.45 GHz) plasma ball under a hydrogen atmosphere at a pressure of 2 kPa. The same discs were also sintered using both non plasma microwave and tube furnace firing. The microwave plasma sintering is very rapid with full disc strength of approx. 1000 N based on 3--point bend tests being achieved within 10 minutes. In contrast the sintering time in the tube furnace involved treatments of up to 6 hours. The non plasma microwave system involved intermediate treatment periods of 1 to 2 hours.

Another advantage of the microwave plasma treatment is that the degree of sintering between the individual nickel powder particles can be precisely controlled by the duration of the treatment time in the plasma. There was a broadly linear increase in fired pellet breaking strength with plasma treatment duration. In addition to breaking load, the mechanical properties of the sintered nickel discs were compared based on Rockwell hardness tests and density measurements. The morphology of the sintered discs was compared using microscopy and SEM.

This study demonstrated that the plasma microwave sintered discs produced similar or superior performance (depending on processing conditions) to discs fired using the non-plasma microwave and furnace firing conditions. Accurate control of the sample conditions and structure can easily be controlled with the plasma system compared with the conventional systems. The apparent volumetric heating in the microwave systems give a more uniform heating at lower temperatures and allows for greater control and homogeneity.

Keywords: Microwave Sintering. Plasma. Nickel, Volumetric Heating

1 Introduction

Nickel can be used for a wide range of commercial products because of its corrosion resistance, wear resistance, mechanical strength, thermal expansion, electrical conductivity and magnetic permeability [1]. Nickel has a melting point of 1453 ºC. It is a principle alloying element for stainless steel. Nickel powder was selected as a suitable material for sintering as it had a relatively low sintering temperature compared with other powders available and was useful for shrinkage comparison and to compare the oxidation during the sintering process, depending on the conditions. The nickel powder was also used as it forms a base for many bonding applications with other materials such as burs or grinding wheels.

1.1 Sintering

Sintering is described as a heat treatment during which a powder mass or powder compact is densified and adopts the desired composition [2]. Weissgerber [3] says that sintering is a step by step process with five distinct steps for production; powder production, powder preparation, forming processes, sintering and post sintering processes. These processes form and sinter a green body into a final sintered body. A wide range of studies have been carried out on microwave sintering, focusing on the volumetric heating aspect of the process, heating from the inside out. There has been significant study of microwave interaction with materials and the type of processing microwave heating can offer [4-9]. Bykov et al. [10] sates that microwave processing is the ability of a material to absorb electromagnetic energy.

Breval et. al [7] explains the need for a less time consuming process and reduce the need for added heat energy. All heat energy, required for the sintering body, must pass through its surface. Agrawal et. al [8] shows that the volumetric heating is very quick and reduces the need for external heat sources. Microwaves are electromagnetic radiation with wavelengths between 1mm and 1m in free space and with frequencies in the range of 300 GHz -- 300 MHz. Standard equipment for industrial or scientific processing operates at a frequency of 2.45 GHz. Comment on microwave plasma

1.2 Microwave Sintering

In the case of microwave sintering, the properties of the material have a greater effect. The dielectric properties of the materials can have an influence on the sintering performance. Ankelkar et al [9] shows that the dielectric property K is a key factor for the microwave absorption characteristics of a material. Materials with a high dielectric loss will couple well with microwaves a room temperature, while materials with poorer loss will require some heating prior to microwave exposure. This type of susceptor heating is generally not required for most powder metals. Susceptor heating is used for achieving uniform heating. Leonelli et al. [11] accounts for the depth of microwave penetration. The magnetic properties of a material can determine the penetration depth of the microwaves. This is a limiting factor for powder production. The higher the conductivity and permeability, the lower the penetration depth the equation below in eq: 1 outlines this. Roy et al. [12] describes the improvements for microwave processing, including finer grain sizes, porosity was more rounded and higher ductility and toughness was also found.

Wroe [13] outlines the features of microwave sintered materials as having significantly faster heating rates than conventional methods as well as operating under lower sintering temperatures. The grain sizes can be significantly smaller and the produced bodies can have greater densification. Saitou [14] also outlines the greater shrinkage rates that can occur from microwave sintering compared with conventional heating techniques. Anklekar [9] indicates the added advantages of improved thermal gradients, higher energy efficiency, improved mechanical properties, novel finer microstructures, reduced atmospheric interaction and lesser environmental hazards. These advantages can vastly improve the cycle time for production and also the energy consumption per process is far more efficient than the alternatives.

$$d = \sqrt{\frac{1}{\pi f \sigma \mu_a}}$$

Where: d= skin depth (m) f = frequency (Hz)
μ_a = microwave wavelength in air (m) and σ = material electrical conductivity ($\Omega^{-1}m^{-1}$)

1.3 Microwave Plasma Sintering

In the case of microwave plasma sintering, the plasma acts as the susceptor and allows the microwave sintering produce uniformly sintered samples. The plasma is instantaneous and produces heat directly to the surface of the sample. This process differs greatly from conventional methods and is extremely quick when compared with the standard processes, thus reducing energy consumption and throughput time. Clark and Sutton [15] outline that when gases are used in microwave sintering, plasma can be formed under certain conditions that are useful for processing. Such gases are used to reduce oxidation of certain materials and to help the microwaves form a plasma. Clark and Sutton further explain that in order to achieve the full benefit of microwave processing, the parameters should be set with the biggest influence on microwave heating performance, instead of the material characteristic's influence.

Microwave plasma sintering establishes a quick and controllable method of sintering with greater densification and uniformity. Energy consumption is dramatically reduced and throughput time is extremely quick. The need for external susceptors is reduced even further than that of conventional microwave. The following experiments aim to show the benefits of microwave plasma sintering.

2 Experimental

The samples used in this comparison study are made from T110 nickel powder obtained from Inco. The nickel powder is supplied ~1 μm in size. These were pressed using a hydraulic press and a 20 mm die.

The samples are pressed and fired over a range of conditions. The samples are pressed into 20 mm discs with 3 g of powder, giving an average thickness of 2--2.5 mm depending on pressing conditions. A range of samples were pressed for each sintering process. the pressing conditions ranges from 100 MPa to 350 MPa in increments of 50 MPa. Three samples were pressed at each condition to show consistent results and for testing and characterisation purposes.

2.1 Microwave Plasma Sintering

The microwave sintering process uses a novel microwave plasma with a hydrogen atmosphere. A 6 KW microwave generator was used at a standard 2.45 GHz microwave frequency. The samples are loaded into the chamber and pumped down to a vacuum. The conditions for firing a plasma require a pressure of 2 KPa under hydrogen atmosphere. The microwaves can be activated once the initial conditions are met. Once the microwaves are turned on, a plasma forms in the centre of the chamber, given a certain percentage power output. The higher the power, the more intense the plasma. The UCD samples were tested at 1.2 KW and 2.4 KW power. The pump down and injection of hydrogen into the chamber can take up to 5 minutes in total. The treatment time was 10 minutes of exposure to microwave plasma. Should the samples require less heating and a shorter sintering duration; the parameters can be altered to a range of conditions. Sintering has been carried out down to 30seconds sintering time. For operation at 1.2 KW, the system could run directly at 1.2 KW for 10 minutes. However for the higher powers, the power would be ramped up in steps, starting at 1.2 KW for 2 minutes, then to 1.8 KW for 3 minutes and finally for 5 minutes at 2.4 KW. This allows for control of the reflective power and prevents plasmas forming in other locations inside the chamber. The samples were fired in batches of three at a time, with constant rotation inside the plasma. The system has an automated controllable rotation system installed. The restriction in the operating size of the plasma ball only allows for up to 5 samples to be treated at one time. At the higher powers the plasma ball increases in size to approximately 5 cm in diameter. Larger systems can be used for such operations but as of yet the system has not been upgraded.

A image of the Microwave Plasma system is shown below:

2.1.1 Sample conditions for Microwave Plasma Sintering

Explanation?

Power (KW)	Pressing Load (MPa)					
1.2	100	150	200	250	300	350
2.4	100	150	200	250	300	350

2.2 Microwave Sintering

Microwave sintering was carried out in a microwave induction heating furnace at EMPA in Switzerland [16]

The samples were fired in a microwave furnace with a 6 KW operating capacity, similar to the microwave capacity of the plasma system. They were fired at three different conditions with a batch of samples prepared in the same way as outlined before and with the same range of pressing loads. Each temperature condition allowed for approx 20-30 samples fired at one time. The samples were held on a SiC substrate, to act as a susceptor, and treated. Susceptors are in general secondary couplers made of SiC or MoSiC as outlined by Roy et al. [12]. Each process took 1-2 hours setup and 15-20 minutes sintering and further 1-2 hour cooling. Whole process took 3-4 hours in total. Higher sintering temperatures would have required longer heating times and soak times.

2.2.1 Sample conditions for Microwave Sintering

Temperature °C	Pressing Load (MPa)					
450	100	150	200	250	300	350
500	100	150	200	250	300	350
700	100	150	200	250	300	350

2.3 Conventional Sintering

The samples that were sintered using the conventional method were sintered in a tube furnace in an argon atmosphere. The samples were prepared as before and sintered at three different temperatures, starting at a low temperature of 450ºC then 750ºC and finally 900ºC. Each batch consisted of three samples fired at the same condition. The heating zone of the furnace only allowed for three to be treated at a given time.

2.3.1 Sample conditions for Conventional Sintering

Temperature ºC	Pressing Load (MPa)					
450	100	150	200	250	300	350
750	100	150	200	250	300	350
900	100	150	200	250	300	350

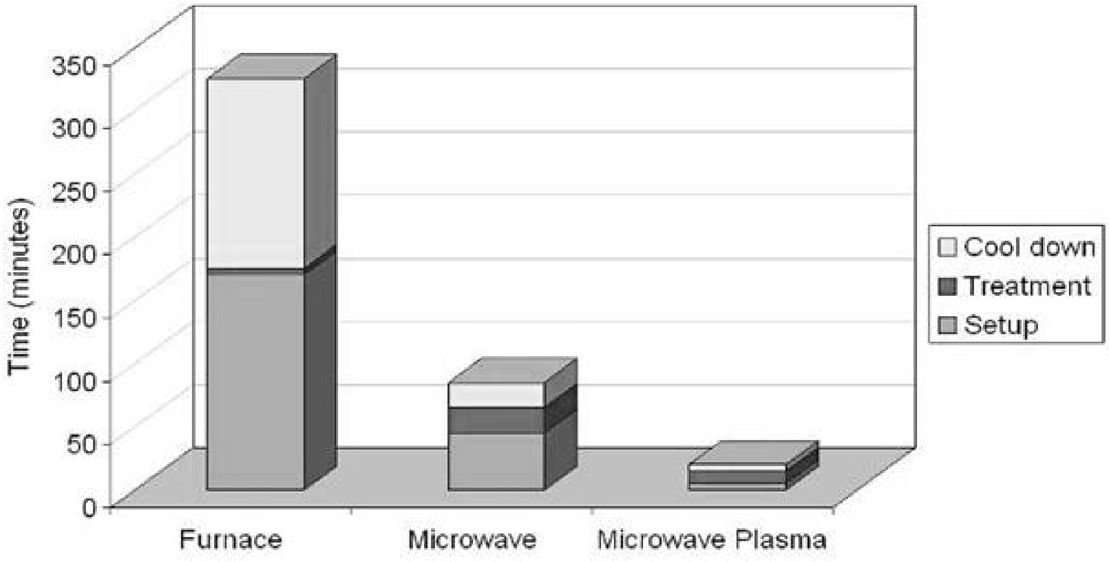
2.4 Characterisation

Each sample was characterised by performing breaking load tests using a 3--point bend setup on a Hounsfield load tester, Rockwell hardness tests using an indenter, SEM analysis using a Hitachi TM--1000 desktop SEM and density measurements using Archimedes's principle in mercury. Some microscopy was also used for sample verification.

3 Results and Discussion

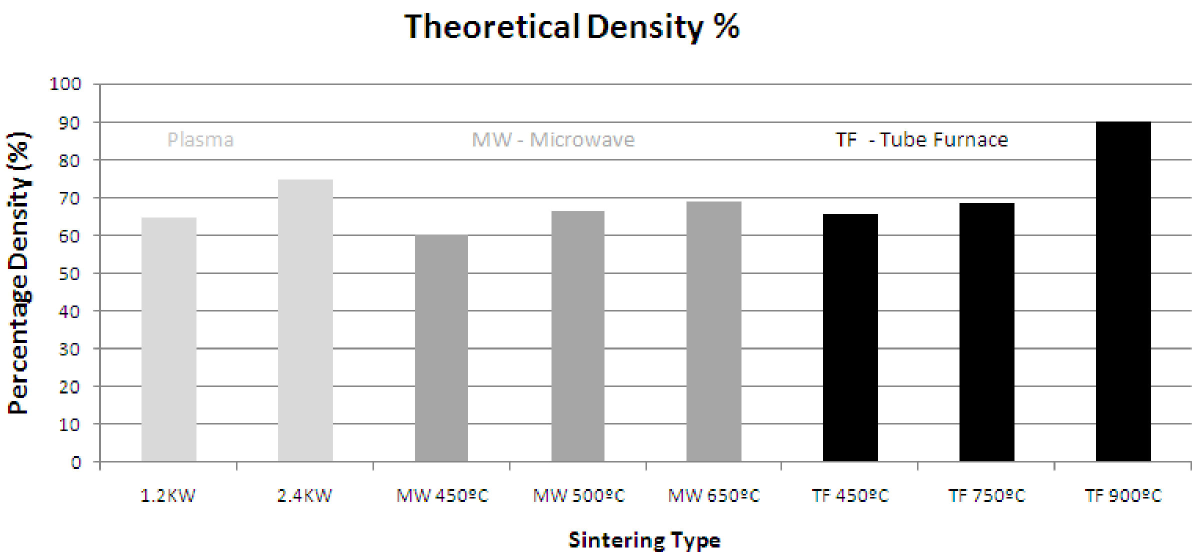
3.1 Results

Sintering times



3.1.1 Density

The density of the samples was measured using Archimedes principle in mercury. The following graph in figure 2 shows the percentage of theoretical density of nickel. The density of nickel is 8.912 g/cm^3. the increase in temperature and power have a corresponding increase in density. The tube furnace sintering shows high levels of density for the 900ºC sample which would indicate the sample has become almost solid and the pore sizes are very small. This value is included as a representation of the density a sample can achieve at the higher temperatures.


Theoretical Density %
Percentage Density (%)
100
90
80
70
60
50
40
30
20
10
0
Plasma
MW - Microwave
TF - Tube Furnace
1.2KW
2.4KW
MW 450ºC
MW 500ºC
MW 650ºC
TF 450ºC
TF 750ºC
TF 900ºC
Sintering Type

3.1.2 Plasma Microwave Sintering

The following graphs show the difference in breaking load for each sintering technique. Above 900 ºC the composition becomes more ductile which conflicts the breaking load tests. The loads below that of 900 ºC compared with density measurements and Rockwell hardness readings.

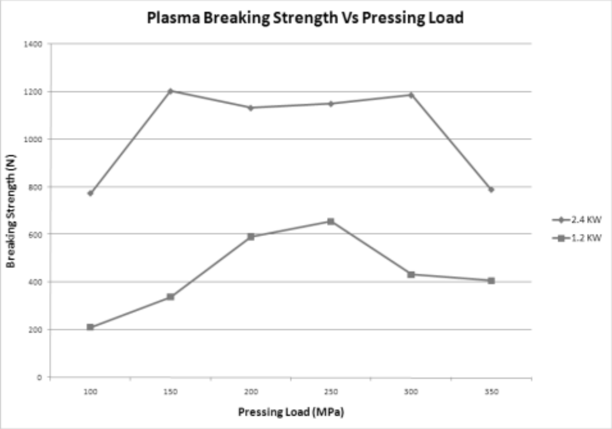


Figure 3: Plasma Sintering Breaking Load

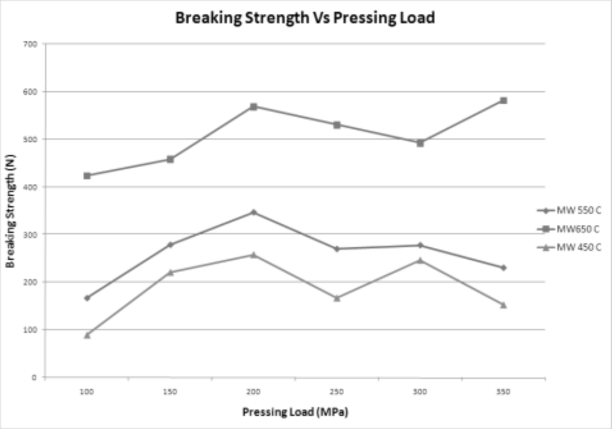


Figure 4: Microwave Sintering Breaking Load

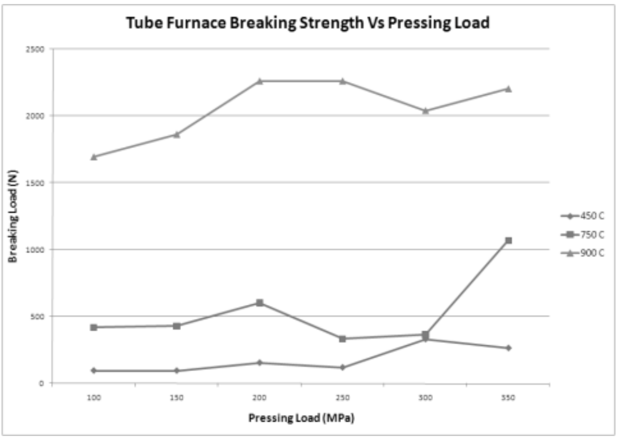


Figure 5: Furnace Sintering Breaking Load

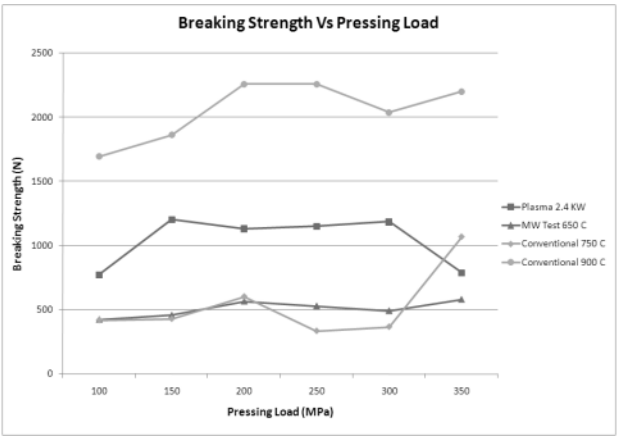


Figure 6: Combined Breaking Load

The following table: 3 outlines the figures obtained through sample characterisation of each sintering technique including the density, percentage theoretical density, Rockwell hardness and fracture toughness.

Sintering Type	Max Density g/cm^3	% Theoretical Density	Rockwell Hardness	Max Breaking Strength (N)
1.2KW	5.8	64.9		407.2
2.4KW	6.7	74.8		788.0
MW 450ºC	5.4	60.1		230.8
MW 500ºC	5.9	66.5		581.8
MW 650ºC	5.5	69.0		152.8
TF 450ºC	5.9	65.8		265.3
TF 750ºC	6.1	68.7		1069.3
TF 900ºC	8.0	90.3		2202.5

Comment on density of the non-plasma microwave 650C being higher then thermal treatment 750C – is this the temperature outside or inside the tube furnace?

3.1.3 Rockwell Hardness

3.1.4 SEM Images

FuiShown below are SEM images taken on a desk--top SEM. each image shows the morphology and heat affected regions of interest. All images display the characteristics of the 300MPa samples. The images compare the structure and agglomeration of each sintering type.

The first three images show the samples at 10,000x magnification.

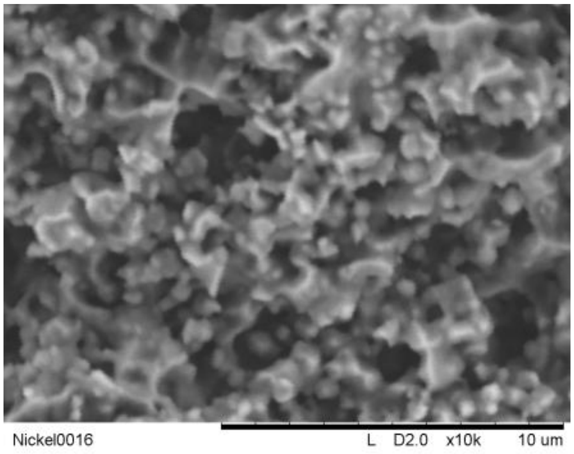


Figure 7: Plasma Microwave Sintered 2.4KW

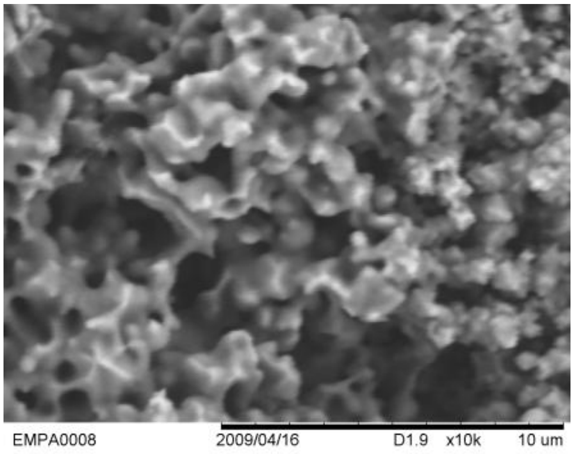


Figure 8: Microwave Sintering 650ºC

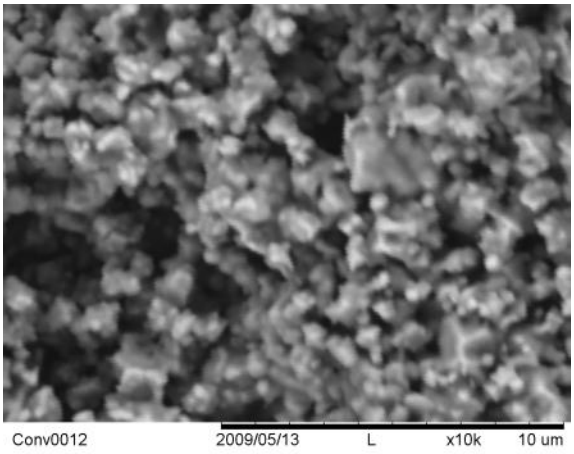
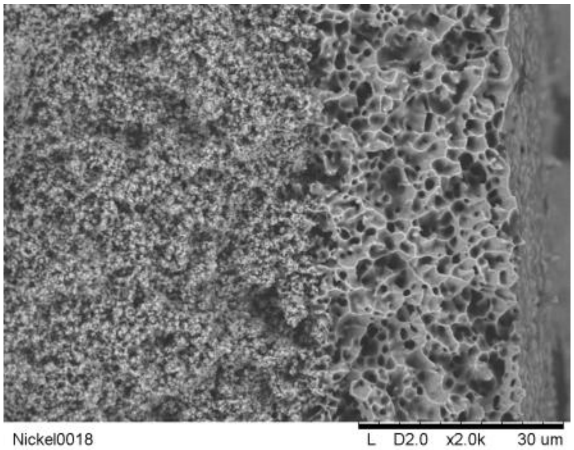


Figure 9: Furnace Sintering 750ºC

The next set of images show the heat affected zones for each sintering method. Each image is taken at 2000x magnification. In each case the top surface is to the right hand side of the image.



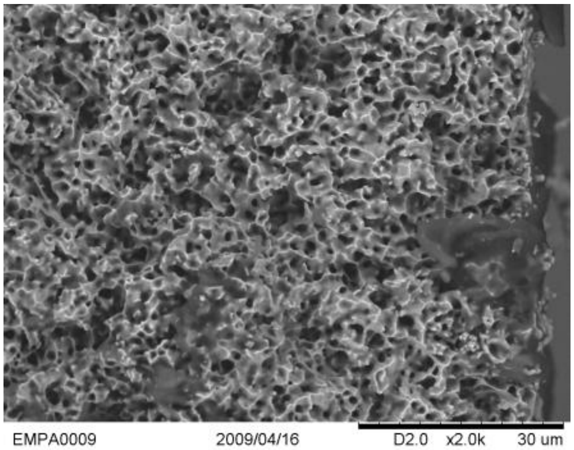


Figure 10: UCD Plasma Sintering 2.4KW Figure 11: Microwave Sintering 650ºC

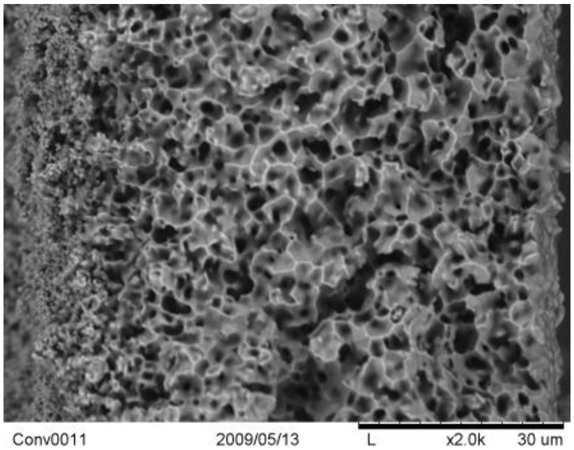


Figure 12: Furnace Sintering 750ºC

3.2 Discussion

The SEM images shown in figures 7-12 describe the difference in processing techniques for each sintering process. The plasma sintered samples show a small heat affected zone on the surface, ~30 µm thick. This zone suggests the plasma is acting as a heat susceptor and causing external heating. The internal heating or volumetric heating, is apparent throughout the higher temperatures as can be seen in figure 8. The plasma samples are more uniform in the centre and show necking occurring even in the middle section. In contrast, the conventional microwave processing produces a thicker heat affected zone ~100 µm as seen in figure 9. This would suggest that the susceptor is having a far greater influence as the middle section shows a gradient from the outer surface towards the centre. More necking occurs nearer the surface and the centre seems more powder--like, shown in figure 10. The conventional samples show similar results and a slightly larger heat affected zone, than that of the plasma but less than the microwave. This would appear to be relating to the heating effect of the induction heaters. Within the sample, shown in figure 12, necking starts to occur gradually but is not quite as uniform or apparent compared with the plasma system.

4 Conclusions

Overall it would seem that the plasma system is closer to the conventional system in terms of heating effect but with greater volumetric heating and little or no significant heat affected zone. The microwave while quick is still slower than the plasma system and requires added heating of the samples for higher temperatures. The plasma system is constrained to size but offers the greater flexibility overall. 40% of microwave plasma power, i.e. 2.4 KW delivers comparable results to between 750 ºC and 900 ºC tube furnace. The majority of necking and particle agglomeration occurs at the higher temperatures and powers. The results of the paper conclude that the standard microwave sintering system is larger and can accommodate more samples per process but is a longer process than the plasma system. The same can be said for the conventional tube furnace. While the results are positive, the time factor and soak time play a big part in the sample production. Partial sintering of the samples in the plasma is also possible within 1-2 minutes which is nearly impossible for the furnace based processes. This outlines the flexibility and speed of plasma production. Energy costs are greatly reduced and the samples have improved heating properties.