

Rapid discharge sintering of nickel-diamond metal matrix composites

Barry Twomey, Aidan Breen, Greg Byrne, Alan Hynes and Denis P. Dowling^a
School of Electrical, Electronic and Mechanical Engineering, University College Dublin,
Belfield, Dublin 4, Ireland
^a(denis.dowling@ucd.ie)

Abstract

There is considerable interest in processing technologies which can lead to more energy efficient sintering of abrasive metal matrix composites. In this study the use of a novel microwave plasma processing technique called Rapid Discharge Sintering (RDS) for sintering nickel-diamond metal matrix composites (MMCs) is evaluated. Nickel-diamond powder composites (80 - 20 % by weight respectively) were uniaxially pressed into 20 mm discs at compaction pressures of 100, 200 and 300 MPa. The discs were sintered using a microwave plasma formed with hydrogen and hydrogen/nitrogen as the discharge gases. For comparison, discs were also sintered using a tube furnace in a gas flow of hydrogen and nitrogen (3:1). Discs pressed to 300 MPa were treated at both 850 and 1000°C. The properties of the sintered nickel-diamond composites were characterised using density, flexural stress, hardness, wear resistance, SEM and XRD. The RDS samples sintered at 1000°C achieved the maximum disc strength of approximately 470 MPa within a 20 minute chamber processing time, compared with 6 hours for furnace sintered samples. RDS samples exhibited increased hardness values and a finer nickel matrix over furnace sintered samples. RDS has shown the ability to process nickel-diamond MMCs without oxidation or graphitisation at higher temperatures. As a result, minimal diamond destruction was observed during abrasive wear testing for RDS samples.

1. Introduction

Plasma sintering has been demonstrated as a rapid and uniform sintering technique since its first reported studies by Bennett et al. [1]. Sintering has been carried out in plasmas generated using microwave, rf or DC power supplies [1-3] and the dominant heating mechanism is associated with ion and fast neutral bombardment. Diatomic gases such as hydrogen or nitrogen or a combination of both are typically used for plasma sintering. Plasma sintering is carried out under vacuum although unlike spark plasma sintering (SPS), there is no external force exerted on the workpiece [4]. There have also been a large number of reports in the literature on the (non-plasma) microwave interaction with materials including the type of processing microwave heating can offer [5, 6]. The ability to penetrate the surface of the workpiece enables rapid volumetric heating in microwave processing, reducing the need for external heat sources [6]. Advantages of non-plasma microwave processing over furnace treatment include finer grain sizes, due to the faster processing times, rounded porosity and higher ductility and toughness [7]. Increased shrinkage rates and decreased grain sizes can be achieved with microwave and plasma processing compared with furnace sintering [1, 8, 9].

This study compares, for the first time, furnace and plasma microwave assisted treatments for the sintering of diamond metal matrix composites (MMCs). Nickel powder was chosen as the test material as it is used in a wide range of engineering components due to its corrosion resistance, wear resistance, mechanical strength, thermal expansion, electrical conductivity and magnetic permeability [10]. Nickel powder is also used as a metal binder for many bonding applications in diamond and carbide machining tools [11]. A report outlining sintering of nickel powder using microwaves showed that despite its ferromagnetism properties, attempts to sinter nickel in a non-plasma, microwave system were unsuccessful due to poor coupling [12]. This caused arcing and plasma formation at the sample edges resulting in hot spots and non-uniform heating. The use of a uniform microwave plasma technique called Rapid Discharge Sintering (RDS) was investigated as a method to sinter nickel and diamond MMCs in this study. Samples were sintered above and below the graphitisation point of diamond and oxidation point of nickel using both the RDS and conventional furnace sintering and the properties of the sintered discs were compared.

2. Experimental Methods

Nickel-diamond MMCs were pressed in a uniaxial 20 mm diameter die at pressures of 100, 200 and 300 MPa. INCO™ nickel (T110) and nickel coated diamond (6-12 μm) from Element Six™ were mixed by weights of 80 and 20 % respectively in a T2F-Turbula for 100 minutes prior to pressing. Density was determined using the Archimedes principle in mercury.

The RDS process was carried out using a Circumferential Antenna Plasma (CAP) microwave system (Figure 1) described in more detail elsewhere [13]. Disc samples (diameter 2 cm) were pressed at 100, 200 and 300 MPa before sintering in a hydrogen plasma at a pressure of 20 mbar. The hydrogen flow rate was maintained at 150 sccm for these samples and the final treatment temperature was 850°C. A second set of discs were pressed to 300 MPa samples before being sintered at 1000°C in the microwave plasma. In order to obtain the higher firing temperature 30 sccm of nitrogen was added to the hydrogen gas while keeping the other operating conditions constant. It has been reported previously that the addition of larger

atomic weight diatomic gases increases plasma sintering temperatures [2]. Three disc samples were sintered in each batch run, the discs were rotated in a plasma ball (diameter approximately 5 cm) located at the centre of the CAP chamber. Input powers of 2.4 kW were supplied from a Mugge microwave power supply operating at 2.45 GHz. Sample temperatures were measured using a LASCON QP003 two-colour pyrometer (Dr. Mergenthaler GmbH & Co, Ulm, Germany). The use of a two-colour pyrometer is expected to eliminate the interference effect of the plasma on the emissivity of the sample as no significant plasma emissions are observed for hydrogen and nitrogen at the operating wavelengths of the pyrometer (1.68 and 1.916 μm) [14]. Rapid heating and cooling rates of 400°C/min were observed in the microwave plasma fired samples. Emission spectroscopy was also carried out on the plasma using an Ocean Optics USB4000 spectrometer. Measurements were carried out to investigate relative changes in the electron density and total light emission of the plasma with increasing applied power.

Furnace sintered samples were initially treated in a Lenton tube furnace at 850°C and 1000°C in a flowing argon atmosphere (flow 200 ml/min.) Despite the use of flowing argon gas during sintering, surface oxidation problems arose and therefore further studies were carried out up to temperatures of 1000°C using an Baird and Tatlock tube furnace system in a cracked ammonia atmosphere (3 H₂: 1 N₂ or 90 : 30 ml/min). Heating rates of 5°C/min were used with the same dwell time of 10 minutes at the maximum temperature. The cooling rate was typically 5°C/min.

Figure 1: Schematic of CAP system with microwave plasma in centre of chamber

Flexural stress tests were carried out using a three point bend test. The span between the bottom pins (9 mm) and the cross sectional area of the fractured samples were used to calculate approximate flexural stress with an average value of three samples taken. Hardness testing was carried out using a Rockwell diamond indenter (HR 15 N scale), with the average value of 12 measurements taken. Rockwell indentation was chosen as the large indent area (\approx 1 mm in diameter) should limit the effect of porosity or diamond reinforcement (\leq 20 μm).

Pin-abrasion testing was carried out to determine the wear resistance of the MMCs. These tests were carried out in accordance with the ASTM G132-95 standard using the pin-on-disc configuration [15]. Samples were mounted on their side edge against 80 grit SiC paper at a constant load of 5 N. The reference material used was 2 mm diameter 316 L stainless steel mounted at an offset of 2 mm to the MMC pin. The linear speed of the pin-holder from the outside to inside edge (250 to 90 mm diameter respectively) of the SiC disc was 6 mm/s while the rotation speed of the abrasive disc was maintained at 28 rpm. This configuration ensures no overlapping between the wear tracks. The abrasive contact time for each test was 30 seconds and a fresh SiC abrasive pad was used for each test. The wear rate was determined by average the volume loss (weight loss/sample density) over a constant sliding distance of 6.87 m. 3 samples were tested for each sintering batch.

X-ray diffraction analysis of the unsintered and sintered powder mix was carried out using a Siemens D500 XRD system over a scanning range of 20 – 100 2θ . A step size and time per step of 0.02° and 0.5 seconds were used respectively. A Hitachi TM-1000 scanning electron microscope (SEM) was used to examine the fracture cross-section of MMC samples after three point bend testing and the abraded surface to determine the effect of abrasive wear on the embedded diamonds.

3. Results and discussion

3.1 Sintering conditions

The pressed nickel-diamond discs were sintered at temperatures of 850 and 1000°C. These temperatures were achieved in the microwave plasma following a 2-4 minute ramp up. This is illustrated in Figure 2 which shows the substrate temperature profile with treatment time. Samples were sintered in sets of three with a 10 minute dwell time at the maximum treatment temperature. A total cycle time of 20 minutes including pump down, firing and cooling was required.

Optical emission spectroscopy was used to monitor the plasma intensity with changes in applied power. The peak shift and full width half maximum (FWHM) of the H_{α} and H_{β} , at 656.3 and 486.1 nm respectively, provide an indication of the electron density in the plasma [16]. As the applied power was increased from 1.2 to 2.4 kW, it was observed that the normalised FWHM and H_{α} / H_{β} peak ratio increased by approximately 6%. This indicates a small relative increase in electron density with increasing applied power. This is coupled with an increase in the overall emission, results in an increase in the volume of the plasma ball. The addition of N_2 into the H_2 plasma increase the substrate temperature from 850 to 1000°C. This corresponded to a 10% increase in the normalised FWHM obtained at the applied power of 2.4 kW. Further increases in temperature can be achieved in a pure nitrogen discharge.

Figure 2: Substrate temperature profile for 1000°C RDS treatment (left) and emission intensity observed in hydrogen/nitrogen plasma (right) with increasing powers

Furnace sintered samples were treated initially in a tube furnace at 850°C and 1000°C in batches of three in a flowing argon atmosphere. Due to complete surface oxidation of the nickel however at 1000°C, further sample batches was sintered in the Baird and Tatlock tube furnace with flowing, cracked ammonia atmosphere of hydrogen and nitrogen (3:1). This system required a total cycle time of just over 6 hours, including heat up and cool down times.

Density measurements were carried out using the Archimedes principle and verified using sample dimensions. As illustrated in Figure 3, there is little difference in the sample density obtained using the two techniques despite a significant difference in total treatment times (20 minutes versus 6 hours). The average increase in density of 18 and 26% was obtained using both the tube furnace and RDS sintered samples after treatment at 850 and 1000°C respectively.

Figure 3: Density of pressed and sintered samples

XRD analysis was carried out on the samples to determine the effect of pressing loads on sintered samples. The main peaks observed for the nickel-diamond powder mix correspond to various Ni peaks (ICDD-pdf card 04-0850), as shown in Figure 4. After sintering however, the diamond peaks at 75.3° and 91.5° appear (ICDD-pdf card 06-0675) for all samples [17]. A peak was observed at 26.5° for all furnace treated samples (850 and 1000°C). This peak corresponds to graphite (ICDD-pdf card 56-0159) [18, 19]. As well as the presence of graphite, samples sintered at 1000°C in an argon atmosphere (tube), exhibited several NiO peaks (ICDD-pdf card 44-1159) [20, 21]. Samples treated in a $H_2:N_2$ atmosphere (tube)

displayed no oxidation, although graphitisation was still observed at 26.5, 42.4 and 54.7°. No evidence of oxidation or graphitisation was observed for RDS treated samples.

Figure 4: XRD plots of unsintered nickel-diamond powder and 300 MPa tube furnace and RDS samples sintered at 850 and 1000°C. \diamond - Nickel; \uparrow - Diamond; Δ - Nickel oxide and \circ - Graphite

3.2 Mechanical behaviour of sintered MMCs

Due to the significant oxidation observed for the tube furnace sintered samples at 1000°C in argon, the mechanical behaviour results will be presented for samples sintered in H₂:N₂ for comparative purposes. H₂:N₂ tube furnace sintered samples outperformed argon treated samples in all tests carried out. Flexural strength values (see Figure 5) were determined using a three-point bend test. Little difference was observed between the two sintering techniques. This is due to the similarity in the cross-sectional area and densities achieved between the both sintering techniques. As a result, the same total surface area of nickel would be expected for each comparative set of samples. Although there are slight differences in the average values, these are not considered to be significant as the average error for these tests was \approx 20%. Samples performed better with increased compaction pressures, most likely stemming from an increase in nickel volume/cross sectional area due to increased sample density. Further increases in strength can be achieved in the same treatment times by increasing the process temperatures.

Figure 5: Flexural stress (left) and hardness values (right) of microwave assisted plasma and furnace sintered samples pressed at 100, 200 and 300 MPa

As shown in Figure 5, RDS samples exhibited significantly higher hardness (\geq 24 %) than all the furnace fired samples. While the data for samples fired at 1000°C in argon is not included in this figure, these discs exhibited a 40 and 53% reduction in hardness than that obtained using the a H₂:N₂ atmosphere of using the RDS technique respectively. This indicates that a possible reason for the decreased hardness may be higher levels of surface oxidation. This conclusion however is not supported by reports in the literature that the presence of a NiO layer may be expected to increase surface hardness [23]. The reduction in hardness may therefore be associated with the coating microstructure. As previously reported for microwave treated samples versus furnace treated samples, thermal equilibrium occurs almost instantaneously enabling sintering to occur in minutes in the case of the former [22]. Examining the cross-sectional area of the nickel-diamond composites (Figure 6 and 7), it can be seen that the RDS treated samples exhibit a much finer microstructure with increased nickel flow and particle necking in between diamond particles (black areas) rather than into larger masses. This is most likely due to the heating rate of \approx 400°C/min versus 5°C/min for RDS over furnace treatment. These heating and equivalent cooling rates can be achieved as the high energy plasma discharge is isolated from the colder surroundings (\approx 30°C) of the discharge chamber. The finer microstructure of the RDS treated samples may thus be the most significant factor influencing the increased hardness values observed [7]. The predominant thermal heating mechanism in the tube furnace produced samples with a harder surface layer and a weakened internal structure. The volumetric heating mechanism in the

RDS process produced a structure with uniform heating throughout. In order to investigate this further, abrasive wear testing was carried out on the MMC samples.

Figure 6: Cross-sectional microstructure of 300MPa pressed RDS (left) and furnace (right) sintered at 1000°C

Figure 7: Fracture cross section of tube furnace (top) and RDS (bottom) samples sintered at 1000°C

Abrasive wear testing was undertaken on RDS and tube furnace sintered samples to determine the wear rate of samples pressed at increasing pressures (100 and 300 MPa) and increasing sintering temperatures (850 and 1000°C), as shown in Figure 8. Volume loss was determined by measuring the average weight loss of 3 samples and dividing by the measured sample density. The sliding distance for each test was 6.87 m. The average deviation in the wear rate observed for the stainless steel reference pin was < 20 %. This is within, or lower than the range of error observed for the MMC samples. For samples sintered at 850°C, the RDS treated samples outperformed the tube furnace sintered samples. For the tube furnace samples, volume loss decreased with increasing compaction pressure and decreased further with an increase in sintering temperature. The further decrease may be the result of both increased sample density and an increase in hardness of samples sintered at 1000°C. As illustrated in Figure 8, little difference was observed in the volume loss of the RDS treated MMC samples, although samples treated at 1000°C exhibited somewhat lower rates than those treated at 850°C. SEM analysis was carried out on the samples sintered at 1000°C to examine for differences in grinding behaviour despite similar wear rates. As illustrated in Figure 9, the diamond particles in the RDS samples were embedded in the nickel matrix. Rounding of the diamond edges and cross-sectional fracture were the main wear mechanisms observed with no evidence of diamond pullout. However, a number of regions showed diamond pullout for tube furnace sintered samples. A large number of diamond particles also exhibited significant micro-fracture due to abrasion. This may be due to the onset of graphitisation in tube furnace sintered samples resulting in a decrease in diamond strength. The increased sintering time has already been shown to increase the flow of nickel in furnace sintered samples. As a result, lower levels of nickel coating may be left on the diamond surface resulting in increased exposure and excessive damage during wear testing.

Figure 8: Volume loss after grinding abrasion tests

Figure 9: Diamond rounding and macro-fracture (--) observed for RDS sintered samples (A and C). Diamond pullout and micro-fracture observed for furnace sintered samples (B and D). Abrasion direction was right to left

4. Conclusions

The firing of nickel-diamond MMCs has been compared by sintering samples with furnace and rapid discharge sintering (RDS) sintering techniques. As the high energy plasma discharge is isolated from the 'colder' surroundings of the discharge chamber, rapid heat up and quenching rates can be achieved resulting in a treatment time reduction of 95 % for batch treatments. Comparable sample densities were observed between the two systems, resulting

in similar breaking strengths observed for both furnace and RDS treated MMCs. RDS samples exhibited increased hardness values, most likely due to the finer microstructure of the RDS samples at sintering temperatures of 850 and 1000°C. A finer nickel matrix is observed throughout the cross-section of RDS treated samples, indicating a more uniform, volumetric heating mechanism.

Furnace sintered samples exhibited significant oxidation and the onset of diamond graphitisation at 1000°C. Despite changing the working atmosphere to H₂:N₂, graphitisation was still observed. Similar abrasive wear properties were observed for all RDS samples. This is most likely due to increased diamond bonding demonstrated by diamond rounding rather than pullout. Although furnace sintered samples sintered at higher temperatures (1000°C) exhibited equivalent wear resistance, the graphitisation and increased diamond exposure associated with these treatment temperatures resulted in considerable diamond damage, thus limiting the use of this technique for such materials.

References

- [1] Bennett CEG, McKinnon NA, Williams LS. Sintering in Gas Discharges. *Nature* 1968;217:1287.
- [2] Lynn Johnson D, Sanderson W, Knowlton J, Kemer E, Chen M-Y. Advances in plasma sintering of alumina. *Science of Sintering* 1988;20:109.
- [3] Lourenço JM, Maliska AM, Klein AN, Muzart JLR. Plasma sintering of unalloyed iron: a study of surface porosity. *Materials Research* 2004;7:269.
- [4] Alvaredo P, Gordo E, Vanmeensel K, Van der Biest O. Manufacturing of Fe-based MMCs by spark plasma sintering (SPS). 17th Plansee Seminar, vol. 3. Reutte, Austria: Plansee Group, 2009. p.GT 41/1.
- [5] Bykov YV, Rybakov KI, Semenov VE. High-temperature microwave processing of materials. *Journal of Physics D: Applied Physics* 2001;R55.
- [6] Agrawal DK. Microwave processing of ceramics. *Current Opinion in Solid State and Materials Science* 1998;3:480.
- [7] Roy R, Agrawal D, Cheng J, Gedevarishvili S. Full sintering of powdered-metal bodies in a microwave field. *Nature* 1999;399:668.
- [8] Wroe R. Microwave sintering coming of age. *Metal Powder Report* 1999;54:24.
- [9] Saitou K. Microwave sintering of iron, cobalt, nickel copper and stainless steel powders. *Scripta Materialia* 2006;54:875.
- [10] Jatkar AD, Tracey VA, Gothard DO, Fischer JJ. Sintering of Nickel and Nickel Alloys. *ASM Handbook*, vol. 7: Powder Metallurgy. ASM International, 1993. p.395.

- [11] Egan D, Engels JA. The use of coated diamonds in diamond impregnated tools. *Industrial Diamond Review*, vol. 04, 2004. p.36.
- [12] S. Charmond DB, C.P. Carry Attempts to Sinter a Fine Nickel Powder in a Microwave Single-Mode Cavity. *Euro Pm2009 Proceedings*, 2009.
- [13] McConnell ML, Dowling DP, Pope C, Donnelly K, Ryder AG, O'Connor GM. High pressure diamond and diamond-like carbon deposition using a microwave CAP reactor. *Diamond and related materials* 2002;11:1036.
- [14] Ralchenko Y, Kramida, A.E., Reader, J., and NIST ASD Team *NIST Atomic Spectra Database* (version 3.1.5). National Institute of Standards and Technology, Gaithersburg, MD., 2008.
- [15] Standard test method for pin abrasion testing. Friction and wear testing. West Conshohocken, PA: American Society for Testing and Materials, 1995. p.145.
- [16] Ashkenazy J, Kipper R, Caner M. Spectroscopic measurements of electron density of capillary plasma based on Stark broadening of hydrogen lines. *Physical Review A* 1991;43:5568.
- [17] Hung C, Lin C, Shih H. Tribological studies of electroless nickel/diamond composite coatings on steels. *Diamond and Related Materials* 2008;17:853.
- [18] Wang L, Zhu X, Zhou J, Ouyang S. Morphology analysis of nickel-boron/diamond electroless deposition. *Journal of Wuhan University of Technology--Materials Science Edition* 2008;23:169.
- [19] Prasad B, Sato H, Enoki T, Hishiyama Y, Kaburagi Y, Rao A, Eklund P, Oshida K, Endo M. Heat-treatment effect on the nanosized graphite -electron system during diamond to graphite conversion. *Physical Review B* 2000;62:11209.
- [20] Liu H, Zheng W, Yan X, Feng B. Studies on electrochromic properties of nickel oxide thin films prepared by reactive sputtering. *Journal of Alloys and Compounds* 2008;462:356.
- [21] Chen H, Lu Y, Hwang W. Characterization of sputtered NiO thin films. *Surface and Coatings Technology* 2005;198:138.
- [22] Breval E, Cheng JP, Agrawal DK, Gigl P, Dennis M, Roy R, Papworth AJ. Comparison between microwave and conventional sintering of WC/Co composites. *Materials Science and Engineering A* 2005;391:285.
- [23] Qi YH, Bruckel P, Lours P. Interfacial toughness of the nickel–nickel oxide system. *Journal of Materials Science Letters* 2003;22:371.

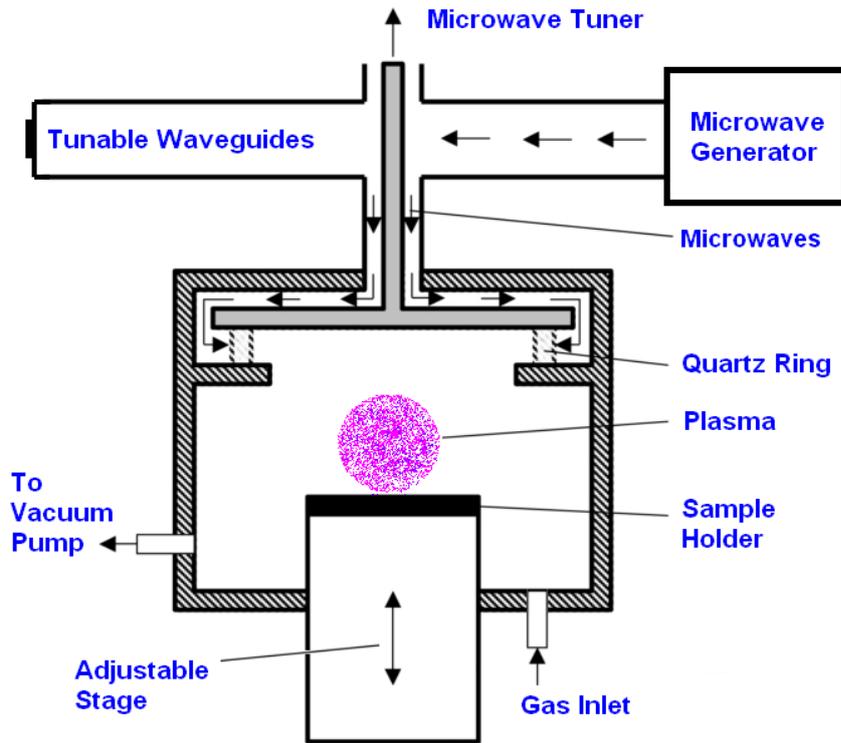


Figure 1

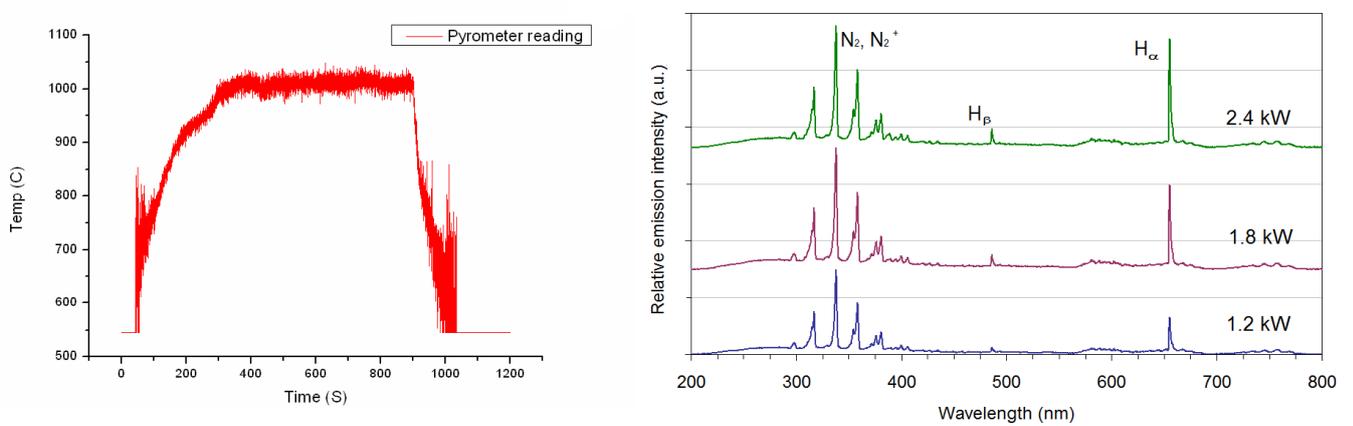


Figure 2

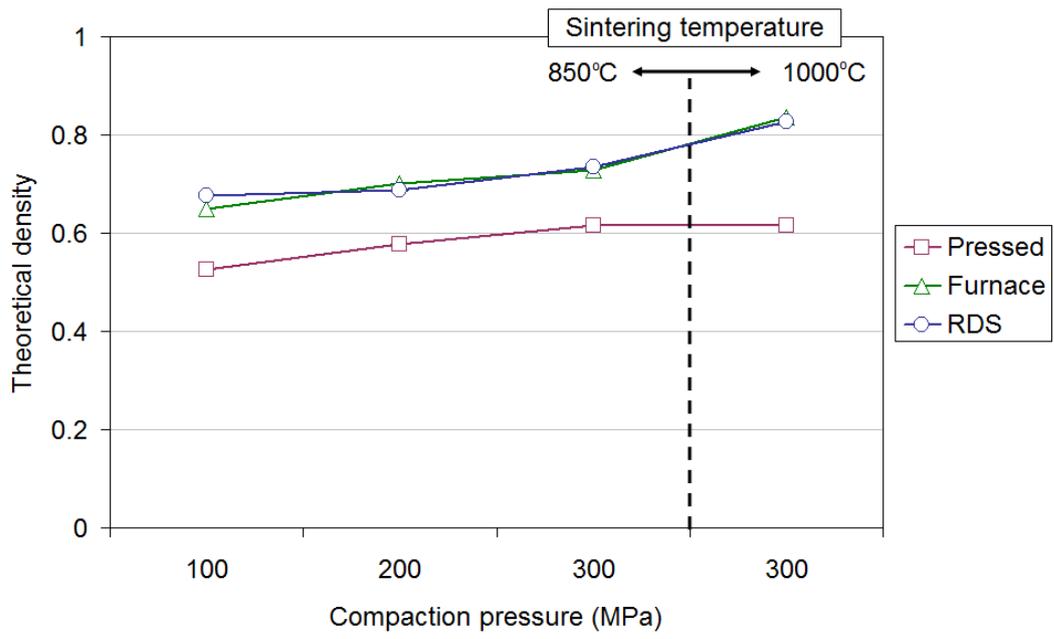


Figure 3

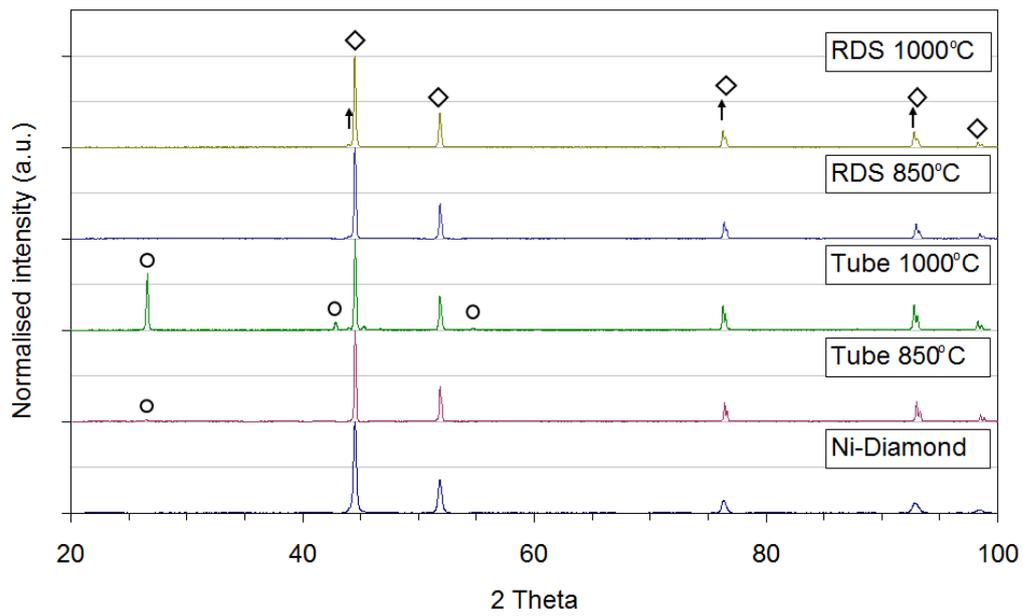


Figure 4

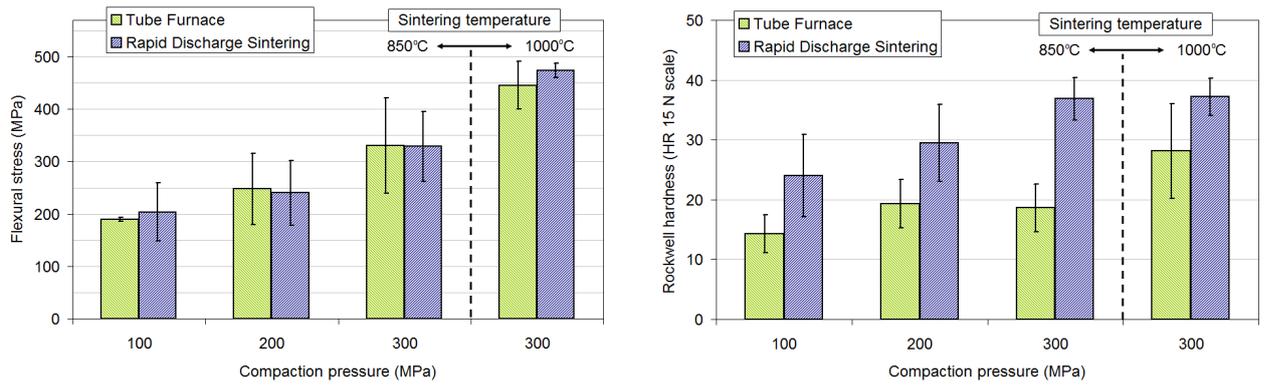
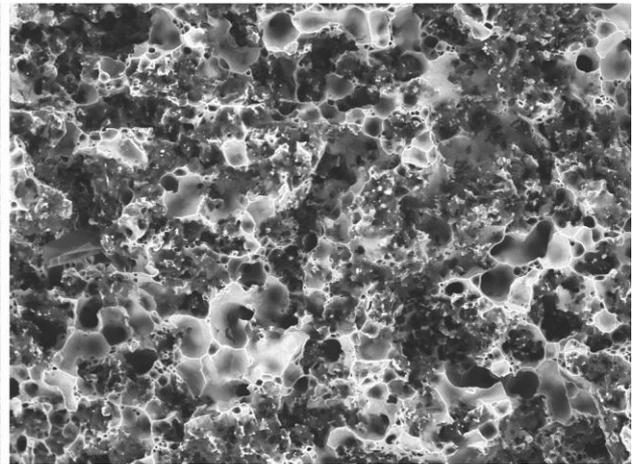
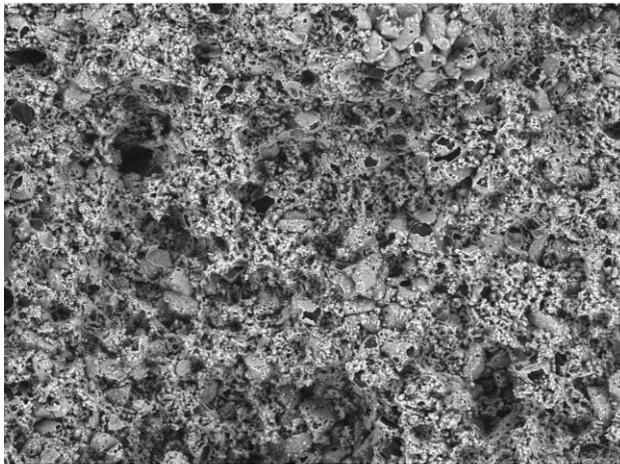


Figure 5

RDS

Tube Furnace

x 1000



x 2500

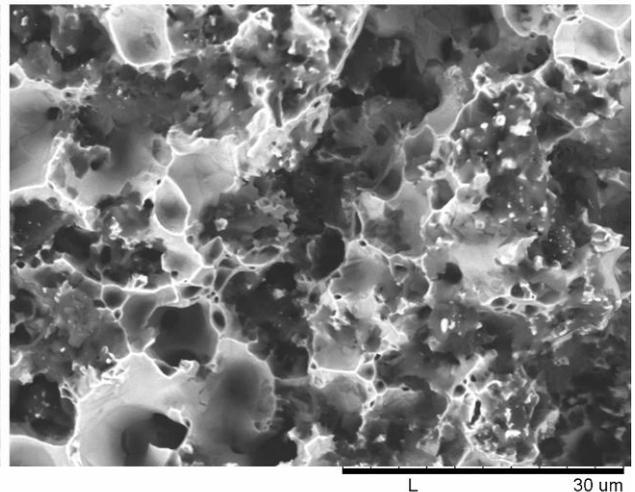
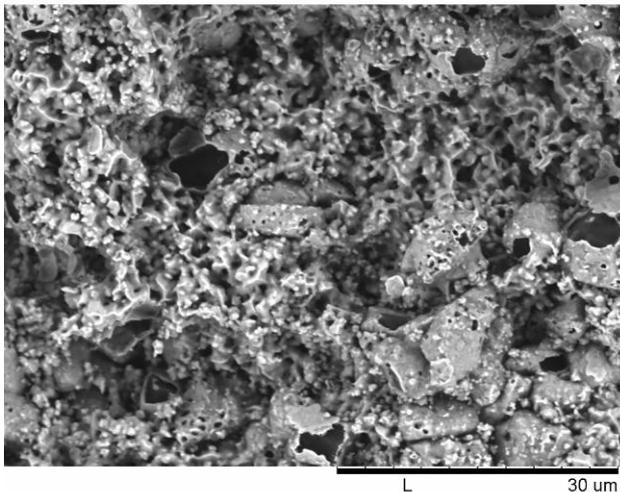
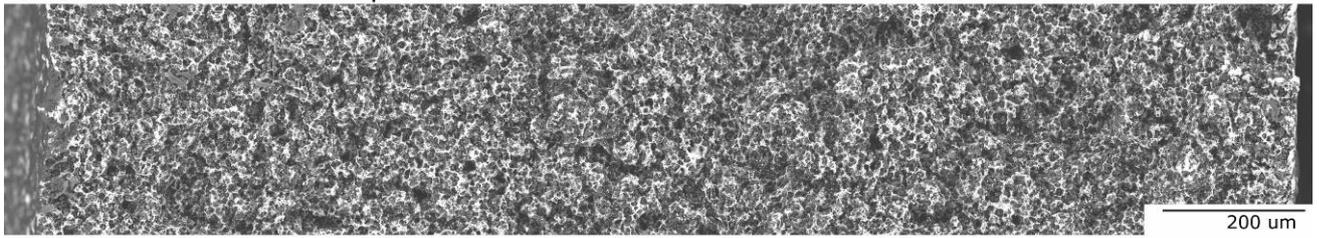


Figure 6

Tube Furnace treated samples at 1000°C



RDS treated samples at 1000°C

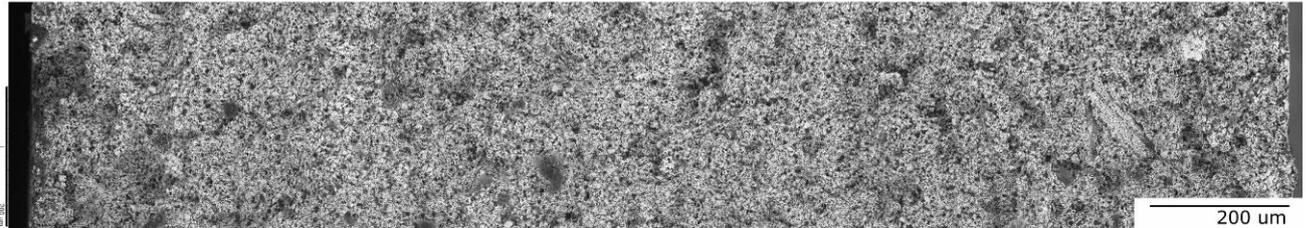


Figure 7

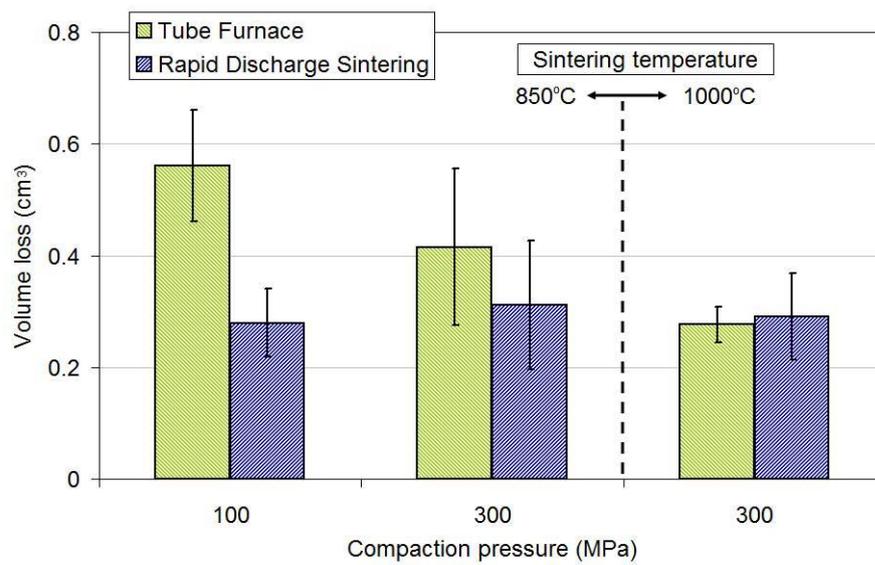


Figure 8

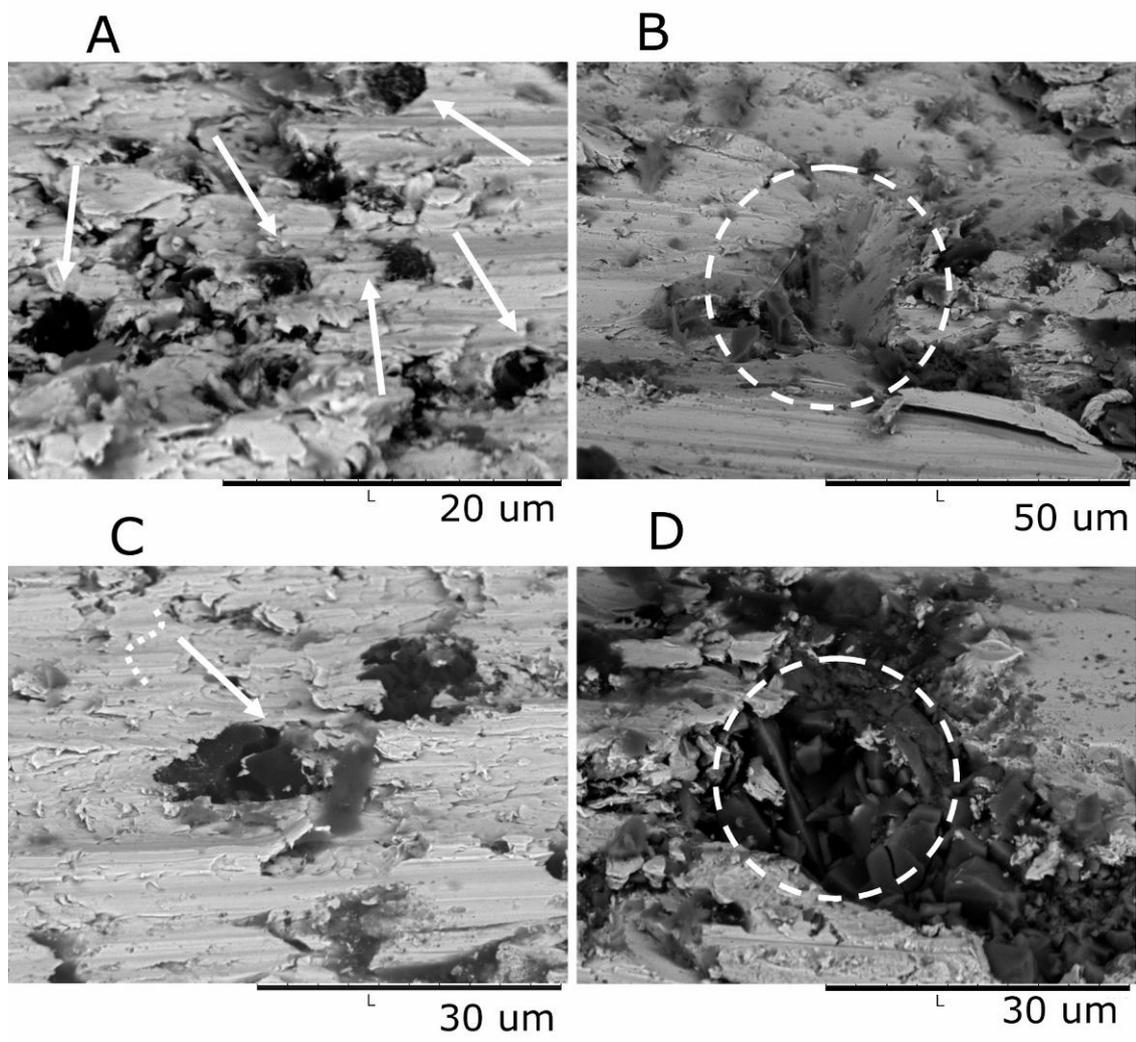


Figure 9