INVESTIGATION OF THE BEHAVIOR OF THE NICKEL CATALYST IN
CHEMICAL VAPOR DEPOSITION SYNTHESIS OF CARBON NANOPEARLS

Dissertation
Submitted to
The School of Engineering of the
UNIVERSITY OF DAYTON

In Partial Fulfillment of the Requirements for
The Degree of
Doctor of Philosophy in Materials Engineering

By
Shanee Danyale Pacley

UNIVERSITY OF DAYTON
Dayton, Ohio
December, 2012
INVESTIGATION OF THE BEHAVIOR OF THE NICKEL CATALYST IN
CHEMICAL VAPOR DEPOSITION SYNTHESIS OF CARBON NANOPEARLS

Name: Pacley, Shanee Danyale

APPROVED BY:

Paul T. Murray, Ph.D.
Advisory Committee Chairman
Professor
Department of Chemical & Materials Engineering

William C. Mitchel, Ph.D.
Committee Member
Senior Scientist
Air Force Research Laboratory

Wiebke S. Diestelkamp, Ph.D.
Committee Member
Associate Professor
Department of Mathematics

Donald A. Klosterman, Ph.D.
Committee Member
Assistant Professor
Department of Chemical & Materials Engineering

Andrey A. Voevodin, Ph.D.
Committee Member
Adjunct Professor
Department of Chemical & Materials Engineering

John G. Weber, Ph.D.
Associate Dean
School of Engineering

Tony E. Saliba, Ph.D.
Dean, School of Engineering
& Wilke Distinguished Professor
INVESTIGATION OF THE BEHAVIOR OF THE NICKEL CATALYST IN CHEMICAL VAPOR DEPOSITION SYNTHESIS OF CARBON NANOPEARLS

Name: Pacley, Shanee Danyale
University of Dayton

Advisor: Dr. Paul T. Murray

Carbon nanopearls (CNPs), also known as carbon spheres and nanospheres, are of interest to the nanoscience community due to their field emission and tribology capabilities. There have been numerous reports on the properties and potential applications of CNPs; however, there have been few studies on the behavior of the catalyst during synthesis. Carbon nanopearls are limited to being used as cold cathodes and lubricants for tribology if the nickel catalyst remains. This research focused on studying the behavior of the nickel catalyst during chemical vapor deposition of CNPs. Carbon nanopearls were grown at various growth times (10 sec, 30 sec, 60 sec, 90 sec, 120 sec and 300 sec) using two different nickel catalyst sizes (20 nm nickel nanoparticles and 100 nm nickel nanoparticles). Chemical analysis was conducted using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). This enabled observation of the chemical phases as growth time increased. Imaging of the CNPs samples was performed using transmission electron microscopy (TEM). Raman spectroscopy was performed to observe the defects and order in the graphitic structures as
growth time varied. The melting temperature of the nickel nanoparticles was investigated experimentally by performing differential scanning calorimetry (DSC) on the nickel catalyst. Theoretically, the melting temperature was calculated using the Gibb-Thomson equation. The question “does the Ni catalyst evaporate during synthesis of carbon nanopearls” was addressed both theoretically and experimentally. Theoretically, the Kelvin effect was used to calculate the vapor pressure of the nickel nanoparticles. The vapor pressure of the nanoparticles was compared to the vapor pressure for bulk nickel, and this helped to determine if the nanoparticles were evaporating. Weight loss experiments were conducted and thermal gravimetric analysis (TGA) was performed on the nickel nanoparticles. These experiments were used to identify the temperature of evaporation. The results from this research showed that during the synthesis process, the Ni oxidized. XRD and XPS showed that the nickel oxide reduced as growth time increased, followed by the formation of a nickel carbide phase. Towards the longer growth times, the carbide decomposed leaving only nickel and graphite. TEM results revealed that the remaining nickel did not exist in the core of the carbon nanopearl, but that it was nickel that had segregated from the CNPs and agglomerated with other nickel particles. DSC identified the melting temperature of the 20 nm nickel nanoparticles to be lower than the bulk melting temperature of nickel. The Gibbs-Thomson effect was used as a guideline for determining the melting temperature of the nanoparticles. Oxidation of the nickel nanoparticles prevented determination of the evaporation temperature. Results from the Kelvin effect indicated that the Ni nanoparticles evaporate sooner than bulk nickel. However, due to XRD identifying Ni at the longer growth times, there was no
evidence to conclude that the Ni had evaporated. Finally, a model for CNPs growth was presented based off the results in this research.
ACKNOWLEDGEMENTS

I would like to acknowledge my Ph.D. advisory committee members for guidance and assistance with preparing my dissertation: Dr. Paul T. Murray (advisor), Dr. William C. Mitchel, Dr. Andrey A. Voevodin, Dr. Donald A. Klosterman, and Dr. Wiebke S. Diestelkamp. In addition, I would like to thank the following people from AFRL/RX (Materials and Manufacturing Directorate) for technical assistance and discussion: Dr. Gail J. Brown, Dr. Kurt Eyink, Dr. Dave P. Anderson, Dr. Howard E. Smith, Dr. Angela Campbell, Kara Storage, Tara Storage, Bob Wheeler, and Carl Liebig.
# TABLE OF CONTENTS

ABSTRACT .................................................................................................................. iii

ACKNOWLEDGEMENTS ............................................................................................. vi

LIST OF FIGURES ........................................................................................................ x

LIST OF TABLES ........................................................................................................... xv

LIST OF ABBREVIATIONS AND NOTATIONS .......................................................... xvi

1. INTRODUCTION ...................................................................................................... 1

2. BACKGROUND ......................................................................................................... 4

   2.1 Natural Carbon Structures .................................................................................. 4

       2.1.1 Diamond ..................................................................................................... 4

       2.1.2 Graphite .................................................................................................... 6

   2.2. Closed Caged Carbon Structures .................................................................... 7

       2.2.1 Fullerenes: Buckyballs (C_{60}) ................................................................. 7

       2.2.2 Carbon nano-onions ................................................................................. 10

       2.2.3 Carbon nanotubes .................................................................................... 13

       2.2.4 Carbon nanopearls ................................................................................... 17

   2.3 Difference Between Carbon Nanopearls and Other Carbon Structures .......... 24

   2.4 Summary of Carbon Structures ........................................................................ 26

   2.5 Catalysts used for Synthesis of Carbon Structures .......................................... 27

       2.5.1 Iron .......................................................................................................... 27
5.1 Chemical Constituents During Growth Time………………………………..50
5.2 Surface Chemical Analysis (XPS)……………………………………………70
5.3 Structure Analysis (Raman)………………………………………………….79
5.4 Melting of Nickel…………………………………………………………….87
   5.4.1 Gibbs-Thomson calculation.............................................91
5.5 Evaporation of Nickel…………………………………………………………93
   5.5.1 Kelvin effect........................................................................97
6. DISCUSSION.....................................................................................100
7. CONCLUSION...................................................................................105
8. FUTURE STUDIES.............................................................................106
REFERENCE LIST..............................................................................107
LIST OF FIGURES

1. Figure 2.1: Cubic diamond structure.................................................................5
2. Figure 2.2: Scanning electron microscopy image of diamond film....................5
3. Figure 2.3: Graphite structure............................................................................7
4. Figure 2.4: Buckminsterfullerene “Buckyball” (C_{60})......................................8
5. Figure 2.5: Typical arc discharge setup for buckyball preparation...................9
6. Figure 2.6: Typical setup for laser ablation.....................................................10
7. Figure 2.7: a) High resolution transmission electron microscopy image of spherical carbon nano-onion; b) high resolution TEM image of faceted carbon nano-onion.................................................................11
8. Figure 2.8: Agglomerated carbon nano-onions that were transformed from nanodiamond. There is an outline of the conductivity path created by the onions.................................................................13
9. Figure 2.9: Carbon nanotube.............................................................................14
10. Figure 2.10: a) The top view of SWCNTs for different roll structures shown in (a)-(c); b) the top view of MWCNTs shown in (d)..............................................15
11. Figure 2.11: a) Armchair SWCNT; b) zigzag SWCNT; c) chiral SWCNT........15
12. Figure 2.12: Typical CVD setup.....................................................................17
13. Figure 2.13: Transmission electron microscope image of carbon nanopearls. This illustrates 3D arrangement of carbon nanopearls........................................18
14. Figure 2.14: High resolution TEM image of carbon nanopearls. Image details concentrically-oriented nano-sized graphitic flakes.................................18
15. Figure 2.15: A diagram of the theoretical growth process of carbon nanopearls.

16. Figure 2.16: a.) Hexagon ring carbon structure with zero curvature, b.) pentagon ring structure with curvature around +60°, c.) heptagon ring structure with outward curvature around -60°.

17. Figure 2.17: High resolution SEM image of carbon nanopearls via CVD process.

18. Figure 2.18: Carbon nanopearls grown over a Ni foil catalyst, using autoclave process.

19. Figure 2.19: Field emission data taken from carbon nanopearls.

20. Figure 2.20: Top-down/tip-growth mechanism of carbon nanotubes on metal nanoparticle (Ni, Co, Fe).

21. Figure 2.21: Top-up/base growth mechanism of carbon nanotubes on metal nanoparticle (Ni, Co, Fe).

22. Figure 2.22: VS mechanism for carbon nano-onion growth. Produces carbon nano-onions with metal core.

23. Figure 2.23: Vapor liquid mechanism for carbon nano-onion growth (no metal core).

24. Figure 4.1: 20 nm Ni nanoparticles, from Sun Innovation, used for all experiments. The picture on the right is a transmission electron microscopy image of the 20 nm Ni nanoparticles.

25. Figure 4.2: 100 nm Ni nanoparticles, from Alfa Aesar, used in all experiments. The picture on the right is a transmission electron microscopy image of the 100 nm Ni nanoparticles.

26. Figure 4.3: CVD Furnace.

27. Figure 4.4: 63.5 mm x 19.05 mm x 9.53 mm quartz boat.

28. Figure 4.5: Rigaku DMAX B horizontal diffractometer XRD.

29. Figure 4.6: X-ray photoelectron spectrometer.

30. Figure 4.7: Renishaw Raman spectrometer.

31. Figure 4.8: Phillips LaB₆ TEM.
32. Figure 4.9: TA Instruments’ Q500 TGA for weight loss analysis……………….47

33. Figure 4.10: Differential scanning calorimeter………………………………….48

34. Figure 5.1: XRD analysis of Ni catalyst before CVD experiments. The 20 nm Ni has a larger peak as a result of the smaller size. Slight shifting in the peaks is due to sample placement in system…………………………………………………..51

35. Figure 5.2: XRD results of carbon nanopearl samples grown using 100 nm Ni, with growth times of the following: 10 sec (top red curve), 30 sec (blue curve, 3rd from top), 60 sec (green curve, 4th from top), 90 sec (purple curve), 120 sec (grey curve) and 300 sec (black curve). The bottom three curves are reference curves……………………………………………………………………………52

36. Figure 5.3: TEM and SAD images of samples grown at various growth times using 100 nm Ni nanoparticles. Left to right, from the top: a) NiO (10 sec), b) SAD pattern with diffraction planes (111), (200) and (220) confirming NiO at 10 sec, c) 90 sec, d) carbon nanopearls at 120 sec, e) carbon nanopearl at 300 sec, f) carbon nanopearls at 300 sec, higher magnification, g) halo ring from SAD of CNPs grown for 5 min, showing amorphous carbon…………………………….57

37. Figure 5.4: XRD analysis of CNPs grown using 20 nm Ni nanoparticles. Bottom three curves are reference curves………………………………………………………59

38. Figure 5.5: Left to right, from the top: a) NiO (20 nm sample at 10 sec), b) SAD pattern, c) 90 sec, d) carbon nanopearls (120 sec), e) carbon nanopearls (300 sec), f) carbon nanopearls at higher magnification showing fridges of carbon flakes at edge, g) SAD of 300 sec CNPs showing amorphous carbon halo……………….63

39. Figure 5.6: XRD analysis of CNPs grown using 100 nm Ni nanoparticles………64

40. Figure 5.7: XRD analysis of CNPs grown at various growth times using 20 nm Ni nanoparticles……………………………………………………………………..65

41. Figure 5.8: XRD analysis of CNPs grown at various growth times using 100 nm Ni nanoparticles………………………………………………………………….66

42. Figure 5.9: XRD analysis of CNPs grown at various growth times using 20 nm Ni nanoparticles……………………………………………………………………..67

43. Figure 5.10: Variation of the NiO phase for each CNPs growth experiment using the 100 nm Ni catalyst, at various growth times The error bars represent variation (standard deviation) of the NiO phase composition from the average composition…………………………………………………………………..69
44. Figure 5.11: Variation of the NiO phase between for each CNPs growth experiment using the 20 nm Ni catalyst, at various growth times. The error bars represent variation (standard deviation) of the NiO phase composition from the average composition. ................................................................. 70

45. Figure 5.12: XPS data on carbon nanopearls grown using 20 nm Ni nanoparticles for 30 sec. Spectra of Ni 2p curve fitting. Inset graph is from referenced literature. ................................................................. 72

46. Figure 5.13: XPS spectra of carbon peaks at 30 sec of carbon nanopearls grown using 20 nm Ni nanoparticles. The small graph is spectra from results found in the literature. ................................................................. 73

47. Figure 5.14: XPS spectra of CNPs sample grown using 20 nm Ni nanoparticles for 60 sec. NiCx peak is increasing. ................................................................. 75

48. Figure 5.15: XPS spectra of CNPs sample grown using 20 nm Ni nanoparticles for 90 sec. NiCx peak at maximum intensity. ................................................................. 76

49. Figure 5.16: XPS spectra of CNPs sample grown using 20 nm Ni nanoparticles for 120 sec. NiCx peak has gotten weaker, and C peak intensity has grown. ........ 77

50. Figure 5.17: XPS spectra of CNPs grown using 20 nm Ni nanoparticles for 300 sec. NiCx peak is no longer visible. Carbon peak is now indicative of graphite being present. Pi shake up at 291 eV verifies graphite present. .... 78

51. Figure 5.18: Raman spectra of CNPs samples grown using the 100 nm at the growth times: 90 sec, 120 sec, and 300 sec. ......................................................... 81

52. Figure 5.19: Raman spectra of CNPs grown using 20 nm Ni for the growth times: 60 sec, 90 sec, 120 sec, and 300 sec. Inset graph is spectra taken from literature. ................................................................. 83

53. Figure 5.20: Average ID/IG for each CNPs experiment grown using the 100 nm Ni, at various growth times. ................................................................. 86

54. Figure 5.21: Comparison of average ID/IG for experiments 1, 2 and 3. ........ 87

55. Figure 5.22: DSC measurements of 20 nm Ni nanoparticles (as is). Results show melting temperature of 366.6 °C. ................................................................. 89

56. Figure 5.23: DSC measurements of 100 nm Ni nanoparticles (as is). Results indicate oxidation occurred as nanoparticles were heated. There is a small dip in the curve around 350 °C, which may indicate a small portion of the sample melted. ................................................................. 90
57. Figure 5.24: TGA of 20 nm Ni nanoparticles. Weight loss of 1.45 % up until 400.35 °C, then gains 1.12 % up until 900.77 °C. The total weight loss for this sample was 0.33 % from the starting weight of 10 mg.

58. Figure 5.25: TGA of 100 nm Ni nanoparticles. Weight loss of 0.79 % up until 400.12 °C, then loses another 0.35 % up until 900.86 °C. Total weight loss for this sample was 1.14 % from starting weight of 10 mg.

59. Figure 5.26: Moisala et al results from vapor pressure calculations using the Kelvin effect.

60. Figure 6.1: Carbon nanopearl growth model.
LIST OF TABLES

1. Table 2.1 Comparison of carbon structures ......................................................25
2. Table 4.1 Weight loss experiments .................................................................49
3. Table 5.1 Growth time experiments ...............................................................50
4. Table 5.2 Relative chemical composition, for each phase and constituent present in CNPs grown at various times. (values are in %) ..................................54
5. Table 5.3 Relative chemical composition, for each phase and constituent present in CNPs grown at various times. (values are in %) ..................................61
6. Table 5.4 Quantitative XPS results of CNPs grown using 20 nm Ni at 30 sec ....73
7. Table 5.5 Quantitative XPS results of CNPs grown using 20 nm Ni at growth times 60 sec - 300 sec (%) ..........................................................78
8. Table 5.6 I_D/I_G and I_2D/I_G for CNPs grown using 100 nm and 20 nm Ni ......82
9. Table 5.7 Average I_D/I_G for CNPs grown using 100 nm and 20 nm Ni in the 2nd and 3rd experiments ...........................................................85
10. Table 5.8 Weight loss measurements (average) in milligrams (mg) ............94
# LIST OF ABBREVIATIONS AND NOTATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aver</td>
<td>Average</td>
</tr>
<tr>
<td>C</td>
<td>Carbon</td>
</tr>
<tr>
<td>CNPs</td>
<td>Carbon nanopearls</td>
</tr>
<tr>
<td>CNTs</td>
<td>Carbon nanotubes</td>
</tr>
<tr>
<td>Co</td>
<td>Cobalt</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>Fe</td>
<td>Iron</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>Multi-wall carbon nanotubes</td>
</tr>
<tr>
<td>Ni</td>
<td>Nickel</td>
</tr>
<tr>
<td>Ni₂O₃</td>
<td>Nickel oxide</td>
</tr>
<tr>
<td>Ni₃C</td>
<td>Nickel carbide</td>
</tr>
<tr>
<td>NiCO₃</td>
<td>Nickel carbonate</td>
</tr>
<tr>
<td>NiO</td>
<td>Nickel oxide</td>
</tr>
<tr>
<td>SAD</td>
<td>Selected area diffraction</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>Si</td>
<td>Silicon</td>
</tr>
<tr>
<td>StDev</td>
<td>Standard deviation</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Sulfur</td>
<td>S</td>
</tr>
<tr>
<td>SWCNTs</td>
<td>Single-wall carbon nanotubes</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermal gravimetric analysis</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>Zn</td>
<td>Zinc</td>
</tr>
</tbody>
</table>
1. INTRODUCTION

Carbon nanopearls (CNPs), also known as carbon spheres and nanospheres, have been of interest to the nanoscience community since R. Smalley and S. Iijima introduced buckyballs and carbon nanotubes \(^{[1,2]}\). These spheres of graphene flakes are reported to have diameters ranging from 60-2000 nm \(^{[1-8]}\). They exhibit field emission properties that would be ideal for cathode materials, and potentially lubricant additives for tribological coatings \(^{[9]}\). Carbon nanopearls have also been reported as potential transporters of proteins, nucleic acids, and drug molecules in the nuclear membrane and across the cell membrane\(^{[10]}\). However, the main area of interest for carbon nanopearls is field emission. In the recent years, carbon nanotubes (CNTs), tubular graphitic sheets, were considered a good material for inexpensive field emission cathodes \(^{[9]}\). However, CNTs field emission properties are highly dependent on their orientation (which is very difficult to control), and emission from CNTs is unsteady \(^{[9]}\). Carbon nanopearls are a better material for field emission purposes because they are not restricted to their orientation, and they have sound and uniform emission \(^{[9]}\).

Synthesis of carbon nanopearls has been performed in many ways, which include: growth from glucose using hydrothermal conditions \(^{[3]}\), non-catalytic chemical vapor deposition (CVD) preparation \(^{[4]}\), de-oiled asphalt \(^{[5]}\), direct pyrolysis of hydrocarbons \(^{[6]}\), and recently CVD growth of carbon nanopearls using Ni catalyst \(^{[7]}\). Following the
growth mechanism in [7], Houston et al., recently reported the growth of carbon nanopearls on a Si substrate by CVD, for potential electronic devices [8]. In this process, Ni catalyst (with an average size of 100 nm) were deposited onto a Si substrate. As a result, carbon nanopearls grew on the Si substrate, with sizes in the range of 500-700 nm. Though carbon nanopearls have been grown using various methods, few, if any studies have focused on understanding the behavior of the nickel catalyst during synthesis of CNPs. Limitations on the use of carbon nanopearls as field emission cathodes and/or tribological coatings can result if the nickel catalyst is still present. It is imperative to understand what happens to the nickel catalyst before this material can be used in applications. The purpose of this study was to investigate the behavior of the nickel catalyst during synthesis of carbon nanopearls. The central question of whether the Ni catalyst evaporates during synthesis of carbon nanopearls was addressed. In order to effectively address this question, experiments were conducted that allowed synthesis of carbon nanopearls at various growth times. Characterization of the experiments in this dissertation required the following: X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy, Raman spectroscopy, differential scanning calorimetry, and thermal gravimetric analysis. Theoretical approaches were also taken using the Gibbs-Thomson effect and the Kelvin effect. The results presented in this dissertation enabled a better understanding of what occurs with the nickel catalyst during synthesis of carbon nanopearls by chemical vapor deposition, and helped to address the question whether the Ni catalyst evaporates during synthesis of carbon nanopearls.

The remainder of this dissertation is presented as follows. Background information on the various types of carbon structures is presented in chapter 2. Also presented in chapter
2 are brief discussions of the Gibbs-Thomson effect as well as the Kelvin effect. The research objectives are described in chapter 3, and experiment methods are described in chapter 4. Results are presented in chapter 5, followed by a discussion in chapter 6, and conclusion and future works in chapters 7 and 8 (respectively).
2. BACKGROUND

2.1 Natural Carbon Structures

2.1.1 Diamond

The first carbon allotrope that will be discussed is diamond. As mentioned in the introduction, diamond is a natural mineral. Diamond is known to be stable at room temperature and atmospheric pressure. The carbon atoms are sp$^3$ hybridized$^{[11,12]}$. Diamond exists in cubic and hexagonal form. Cubic diamond is the most common form (fig. 2.1)$^{[13]}$. A picture of diamond film is shown in figure 2.2. Face-centerd cubic (FCC) is the crystal lattice for what is referred to as “normal” diamond$^{[12]}$. The FCC diamond structure has eight atoms in the unit cell. This structure is similar to the zinc blende structure. Instead of Zn and S atoms occupying the crystal structure, carbon atoms take these positions; making each carbon atom bonded to four separate carbon atoms. The bond length between these atoms is 0.1545 nm. Along with it being the hardest known natural material (there are some synthetic materials, such as fullerenes, with higher hardness), diamond also has many other great properties: high thermal conductivity, transparent in the visible and infrared, low electrical conductivity, great semiconductor, high index of refraction, and is very lubricious in air. However, due to the rarity of this material, diamonds are extremely expensive. A substitute for diamond was created in 1976, known as cubic zirconia$^{[13]}$. This material is similar to diamond because it is hard,
can be made colorless, and is durable. Cubic zirconia is also cheap to synthesize, and is therefore cost efficient. Nevertheless, cubic zirconia does not have all of the great properties that diamond contains. Overall, diamond is a very rare naturally existing material with great properties. When diamond is heated to temperatures above 3750° C at a constant pressure of 1840 psi, it becomes graphite. This leads us to the next carbon allotrope to be discussed.

![Cubic diamond structure](image1)

**Figure 2.1:** Cubic diamond structure\(^{[13]}\).

![Scanning electron microscopy image of diamond film](image2)

**Figure 2.2:** Scanning electron microscopy image of diamond film\(^{[13]}\).
2.1.2 Graphite

There is another natural occurring carbon material, known as graphite. In contrast to diamond, graphite has only three surrounding carbon atoms[^11]. The graphite structure has planar layers of carbon atoms, which look similar to a honeycomb structure (carbon atoms form hexagon networks resembling honeycomb). This can be seen in figure 2.3. In addition to the different neighboring carbon atoms between diamond and graphite, there is also a difference in their hybridization. Diamond is sp\(^3\) and graphite is sp\(^2\) hybridized[^11-15]. Graphite has a strong covalent bond between the carbon atoms in-plane. However, between the planes there is a weak van der Waals bonding. This van der Waals bonding is why the planes can easily slide past each other. The graphite structure can be arranged in different stackings. The two common stacking arrangements of graphite are: ABCABCAB and ABABAB. The ABAB stacking is more stable than the ABCABC stacking due to the shorter carbon-carbon distance in the ABAB[^11-15]. Graphite has great properties, which include: thermodynamically stable, electrically conductive, opaque, great lubricating properties, and great insulating properties along the z-axis. Diamond and graphite are the only natural occurring allotropes of carbon. However, there are several synthetic carbon allotrope materials that are of great interest due to their properties and potential applications. These will be discussed in the following sections.
2.2 Closed Caged Carbon Structures

2.2.1 Fullerenes: Buckyballs ($C_{60}$)

Fullerenes are caged-like carbon materials. There are various types of fullerenes, but only one type will be discussed in this paper. The first type of fullerene discovery dates back to 1970, by E. Osawa\cite{osawa1970}. However, credit to the discovery of the first type of fullerene was given to a team of scientists (H. W. Kroto, J. R. Heath, S. C. O’Brien, R. F. Curl and R. E. Smalley) at Rice University-in 1985, during an experiment to understand how a long-chain of carbon molecules was formed in space (in circumstellar shells)\cite{osawa1970,kroto1985}. The experiment consisted of vaporization of carbon molecules by laser irradiation of graphite. Following time-of-flight spectrometry, clusters of sixty carbon atoms were discovered. This caged structure of carbon atoms was referred to as $C_{60}$, otherwise known as buckyballs (fig. 2.4). The word buckyball is a shortened version of the word buckminsterfullerenes. The name comes from the famous architect, Richard Buckminster Fuller, known for his geodetic dome structures. These geodetic dome structures were very similar to the buckyball (and other fullerene) structures. Often compared to a soccer
ball, the buckyball is a truncated icosahedron\cite{16}. The buckyball structure has 20 hexagons and 12 pentagons. There is a carbon atom at the vertices of each polygon, and a bond along the edges of the polygon. The buckyball has a $sp^2$ hybridization, with some $sp^3$ hybridization (a result of the high curvature)\cite{1,11}. Buckyballs show great mechanical, electrical and thermal conductivity. Promising applications include: cosmetics, field emitters, and superconducting materials\cite{11,12}.

Since their discovery, there has been various ways found to prepare buckyballs. These preparation methods include (but are not limited to): pyrolysis of hydrocarbons, partial combustion of hydrocarbons, arc discharge, laser ablation, resistive heating, and rational syntheses. Arc discharge and laser ablation are the two most common preparation methods. These methods will be discussed in the following sections.

![Buckyball](image)

Figure 2.4: Buckminsterfullerene “Buckyball” ($C_{60}$)\cite{17}.

2.2.1.1 Arc discharge

The first synthesis method to be discussed was arc discharge. This process produces buckyballs by applying high voltage (DC voltage) between two graphite rods (anode and cathode), which are slightly separated\cite{11,12}. The anode is usually longer than the cathode with diameters of 6 mm and 9 mm, respectively. As a result of applying the voltage, arcing (plasma) occurs between the graphite rods. Electrons then collide into the
anode rod, and the rod heats up and evaporates. A carbon-based smoke, containing fullerenes, is formed and deposits on the cathode during cool down. A typical setup of this method can be seen in figure 2.5. An estimated 15% of the particles are fullerenes, with 80% of the fullerenes being $C_{60}$ (buckyballs). The arc discharge method led to the discovery of carbon nanotubes, which will be discussed later on in this review. The next buckyball preparation method to be discussed is laser ablation.

![Figure 2.5: Typical arc discharge setup for buckyball preparation[12].](image)

2.2.1.2 Laser ablation

This was the first method used when buckyballs were discovered at Rice University. Laser ablation is a simple process that involves blasting a pulsed laser beam (the original experiment used a 532nm laser at 30-40 mJ) onto a graphite disk, in an inert gas atmosphere (e.g., He)- high temperature reactor[1,12]. The vaporized carbon sample is collected from the walls of the chamber and then characterized. A diagram of a typical laser ablation setup can be seen in figure 2.6. This method is currently still used in buckyball preparation.
2.2.2 Carbon nano-onions

Carbon nano-onions are closed- spherical carbon cages (fullerenes) that exist inside one another (see fig. 2.7) \[12\]. They are often referred to as multilayered carbon nanotubes that have a length of zero. Some carbon nano-onions have a faceted structure as well (also fig. 2.7). These concentrically arranged shells have a structure similar to an onion. The diameter increases from the core to the outer shell, and the inner shell can have an average diameter of 0.7-1 nm, which is similar to the diameter of a buckyball \((C_{60})\)[19]. The distance between the shell layers is around 0.34 nm. Carbon nano-onions can have a double shell structure (only two layers of fullerenes) or multiple layers of fullerenes. For carbon nano-onions with a faceted structure, the inner shell can be large when compared to the inner shell of spherical carbon nano-onions. These faceted structures consist of shells of metal nanoparticles, inside a carbon structure\[^{12}\]. Bonding within the single layers is covalent for both types of carbon nano-onions. However, the bond between the shells is a Van der Waals force. This bonding is similar to the graphite structure. Carbon nano-onions are made up of sp\(^2\) hybridized carbon atoms. However, there is some evidence of sp\(^3\) hybridized carbon atoms when carbon nano-onions are
made from nanodiamond clusters (this method is mentioned below as a preparation method of carbon nano-onions). Carbon nano-onions were discovered by D. Ugarte. Ugarte discovered that electron irradiation of fullerene soot particles produced multilayered fullerenes, or carbon nano-onions\(^{[20,21]}\). Aside from electron irradiation, carbon nano-onions can be produced using the following methods (but production is not limited to these methods): arc discharge, laser ablation, heat treatment of nanodiamond, RF plasma chemical vapor deposition (CVD), and annealing soot or diamond nanoparticles in vacuum\(^{[12,22-28]}\). Faceted carbon nano-onions can be obtained by heat treating carbon nano-onions (at high temperatures). Chemical vapor deposition is a common preparation method for carbon nanomaterials, and can be used for carbon nano-onion synthesis. This method is explained in details in section 2.2.3.1, under the discussion of carbon nanotubes.

![Figure 2.7: a) High resolution transmission electron microscopy image of spherical carbon nano-onion; b) high resolution TEM image of faceted carbon nano-onion\(^{[12]}\).](image)

Currently, carbon nano-onions lack commercial applications. This is mainly due to the difficulty in preparing large quantities of the material. However, their small spherical shape and van der Walls bond between the shells make their layers easy to
break down \cite{28-31}. As a result, carbon nano-onions can potentially be good lubricants, making them ideal candidates for tribological applications. Other proposed applications include catalysis, and photovoltaic applications\cite{12,28-31}. Due to the lack of large quantities of carbon nano-onions being produced, there have been no reports on the mechanical properties, and very little information on the electronic and thermodynamic properties has been observed. Experiments show resistance measurements of near $0.3 \, \Omega\, \text{cm}$ for carbon nano-onions grown by heat treating nanodiamond\cite{12}. The resistance began at $10^9 \, \Omega\, \text{cm}$ for nanodiamond, and decreased to $0.3 \, \Omega\, \text{cm}$ (or below) when the nanodiamond had completely transformed to carbon nano-onions. The model in figure 2.8 shows what carbon nano-onions look like that have been transformed from nanodiamond via heat treating. The carbon nano-onions are agglomerated, and are held together by carbon-carbon bonds and graphene layers. Reportedly, it is these graphene layers and C-C bonds that produce conductive routes within the carbon nano-onion agglomerates. Currently, the only information provided on thermodynamic properties (besides their transformation to faceted nano-onions when heat treating spherical nano-onions) of carbon nano-onions has been provided by K.W. Street and M. Marchetti in their publication on carbon nano-onion tribological behavior\cite{29}. These authors report that up to temperatures around $750 \, ^\circ\, \text{C}$, faceted carbon nano-onions show thermal stability. Carbon nano-onions are very similar to carbon nanopearls in structure and some of the potential applications. This will be discussed in section 2.2.4. The next carbon nanomaterial to be discussed is carbon nanotubes.
Figure 2.8: Agglomerated carbon nano-onions that were transformed from nanodiamond. There is an outline of the conductivity path created by the onions\textsuperscript{[12]}.

### 2.2.3 Carbon nanotubes

Carbon nanotubes (CNTs) are closed tubular structures containing single or layered graphene sheets of sp\textsuperscript{2} bonded carbon atoms (see fig. 2.9)\textsuperscript{[32,33]}. They were discovered in 1991 by Sumio Iijima, during an experiment using arc discharge to obtain fullerenes\textsuperscript{[13]}. Iijima was studying the different soot types produced during this experiment and noticed (under a transmission electron microscope) cylindrical graphene sheets with multiple layers. Carbon nanotubes are comparable to the structure of fullerenes (C\textsubscript{60}). Cutting a C\textsubscript{60} fullerene equally into two halves at the middle, and joining the two halves with a graphitic cylindrical hollow tube would result in a carbon nanotube structure\textsuperscript{[34]}. The difference between the structure of carbon nanotubes and fullerenes is that fullerenes have a spherical symmetry, while carbon nanotubes have a cylindrical symmetry. These nanotubes are similar to carbon nano-onions in that carbon nanotubes can have multiple layers. These multiple layered nanotubes are called multi-wall carbon nanotubes (MWCNTs). Following the discovery of the MWCNTs, single-wall carbon nanotubes (SWCNTs) were discovered after the growth parameters were changed in the
arc discharge procedure. Reich et al., reported single-wall carbon nanotubes having mean diameters of 1.0-1.5 nm (fig. 2.10a)[34]. Multi-wall carbon nanotubes can have diameters that are about several thousand times larger than single-wall carbon nanotubes (fig. 2.10b). Both SWCNTs and MWCNTs are made up of sp² hybridized carbon-carbon bonds. Carbon nanotubes have unique but different electrical properties depending on the direction they are rolled[35]. There are three roll types: armchair, zigzag and chiral, as shown in figure 2.11. Zigzag tubes have a zigzag formation of the carbon bonds down the length of the carbon nanotubes (fig. 2.11b). When the carbon bonds are normal to the length of the tube, this is referred to as armchair type (fig. 2.11a). Carbon nanotubes that have both zigzag and armchair bonding are chiral (fig. 2.11c). The roll type can be determined based off of the chiral vector. The circumference can be determined based on the magnitude of the chiral vector. The chiral vector is perpendicular to the direction of the carbon nanotube axis.

Figure 2.9: Carbon nanotube[36].
Carbon nanotubes have great electrical and mechanical properties. The electrical properties are dependent on the nanotube’s roll type. Armchair carbon nanotubes have metallic properties; and zigzag nanotubes have semiconductor properties\[^{38}\]. As the diameter of a SWCNT or the outer wall of the MWCNT increases, the bandgap decreases\[^{39}\]. This only applies to zigzag type CNTs. It is these properties that make the
carbon nanotubes interesting candidates for electrical applications, such as field emitters. The company Samsung illustrated the use of carbon nanotubes for electrical purposes by making devices with carbon nanotubes for field emission\(^{40}\). In 1999, Samsung developed the first prototype of a carbon nanotube equipped television display\(^{41}\). Carbon nanotubes are very small in diameter, long in length, and conductive\(^{37}\). The mechanical properties of carbon nanotubes are significant as well. Carbon nanotubes are considered to be the strongest synthetic material known, comparable to diamond\(^{42}\). The theoretical tensile strength of MWCNTs (the outer shell) is about 100 times more than the tensile strength of aluminum\(^{40}\). These nanotubes are expected to have a high elastic moduli (about 1 TPa)\(^{43}\), low density, and have great specific strength properties when used in composites\(^{40}\). It is these mechanical properties that enable carbon nanotubes to be a great candidate material for space applications, chemical sensing, reinforced polymers, and nanobiotechnological applications\(^{42}\).

2.2.3.1 Chemical vapor deposition

There are a few methods used to synthesize CNTs, some of which have been mentioned for preparation of buckyballs and carbon nano-onions (e.g., arc discharge, laser ablation). Chemical vapor deposition is one of the methods used for CNT synthesis that has not been discussed. This process produces CNTs by using a metal catalyst (such as Ni, Co, or Fe) along with thermal breakdown of a hydrocarbon vapor. The substrate (usually a quartz material) is exposed to the catalyst, which is deposited on the surface. The reaction of the hydrocarbon vapor occurs over the catalyst. The common CVD process setup can be seen in figure 2.12. Inside the apparatus there is a preheater and
furnace (combined in one unit), and a quartz tube reactor as well. A hydrocarbon source (e.g., xylene-ferrocene, acetylene, or ethylene) is pumped into the preheater which is at a temperature of about 200°C. The CNTs (typically MWCNTs) develop in the furnace of the CVD setup, usually in a temperature range of 600 to 1000°C, by way of a gas (e.g., Ar/10% H₂) that carries the hydrocarbon to the furnace⁴³. The catalyst absorbs the carbon from the hydrocarbon gas source, and subsequently CNTs are grown. This same procedure is used to produce buckyballs, carbon nano-onions, and carbon nanopearls (which will be discussed in section 2.2.4). The parameters and gas type may be changed for the type of carbon nanomaterial to be prepared. Chemical vapor deposition enables production of large quantities of CNTs, with a reported length up to 2 mm. This growth method is the ideal method for producing high yield-aligned CNTs.

![Figure 2.12: Typical CVD setup](image)

### 2.2.4 Carbon nanopearls

The name carbon nanopearls was coined by a team of scientist at the University of Lyon in 2004. However, carbon nanopearls are no different from the carbon nanospheres that have been around for quite some time. The only difference is the growth methods used and the size. As mentioned previously, these spheres of graphene flakes are reported
to have diameter sizes ranging from 60-2000 nm\(^\text{[1-8]}\). Carbon nanopearls are defined as monodisperse nanospheres of nanocrystalline carbon that form a 3-dimensional arrangement similar to a string of pearls (figure 2.13\(^\text{[7]}\)). These sp\(^2\) hybridized carbon spheres are made up of concentrically-oriented nano-sized graphitic flakes, that are 2-dimensional (see figure 2.14).

Figure 2.13: Transmission electron microscope image of carbon nanopearls. This illustrates 3D arrangement of carbon nanopearls\(^\text{[7]}\).

Figure 2.14: High resolution TEM image of carbon nanopearls. Image details concentrically-oriented nano-sized graphitic flakes\(^\text{[7]}\).
According to A. Levesque et al., carbon nanopearls grow in the following process: the acetylene gas decomposes into atomic carbon (fig. 2.15), a wavy 2D structure of graphene flakes are formed, and the flakes cluster together in a layered manner forming a spherical shape[7]. Reportedly, these 2D flakes are around 4 nm (fig. 2.15). Furthermore, it is reported that there are some amorphous areas present between the layered flakes. Levesque et al., propose that the spherical shape is derived from the combination of pentagonal and heptagonal rings with a planar hexagonal structure, which make up the wavy 2D flakes.

Figure 2.15: A diagram of the theoretical growth process of carbon nanopearls[7].
The structure of each graphitic flake (making up the sphere) consists of graphitic carbon rings (e.g., hexagon, pentagon, and heptagon), and the curvature of the sphere is due to the modulation of the graphitic lattice (see fig. 2.16 for graphitic rings)\textsuperscript{[44]}. Hexagonal carbon rings make a flat sheet (i.e., graphene). The pentagonal rings force the hexagonal rings to curve inward (+60°). Heptagonal rings do the opposite of pentagonal rings. The heptagonal rings force the hexagonal lattice to curve outward (-60°). If there were no heptagonal carbon rings present, the pentagonal carbon rings would form a faceted polyhedron\textsuperscript{[44]}. As a result, the existence of both a pentagonal and heptagonal ring in a hexagonal lattice enables a carbon sphere, with a reduction in the curvature of the structure. There are 12 pentagonal carbon rings needed to form a closed structure (without the presence of heptagonal and octagonal rings)\textsuperscript{[45, 46]}. The number of hexagonal rings is random. This conclusion was derived from the following expression, also known as Euler’s theorem\textsuperscript{[45]}:

\begin{equation}
V - E + F = \chi \tag{2.1a}
\end{equation}

\begin{equation}
\chi = 2 - 2g \tag{2.1b}
\end{equation}

This theory states that for a polyhedron (in this case a sphere), with $F$ faces, $V$ vertices, and $E$ edges $V - E + F = \chi$. Here $\chi$ is the Euler’s characteristic, and $g$ is the genus\textsuperscript{[45]}. The genus for a sphere is zero, which leads to the equation:

\begin{equation}
V - E + F = 2 \tag{2.2}
\end{equation}

As mentioned earlier, carbon nanopearls are made up of pentagonal and heptagonal rings. For a graphitic network made up of pentagonal, hexagonal, heptagonal, or octagonal rings- the edges $E$ are shared by two different polygon faces, and at each vertex $V$ there
are three polygons. Therefore, if $N_n$ represents the number of polygons containing $n$ sides and vertices, Euler’s theorem now becomes\textsuperscript{[45]}.

\[F = N_5 + N_6 + N_7 + N_8\]

\[2E = 3V = 5N_5 + 6N_6 + 7N_7 + 8N_8\]

therefore,

\[(2.3)\quad N_5 - N_7 - 2N_8 = 6 \chi = 12 (1 - g)\]

or, for a sphere

\[(2.4)\quad N_5 - N_7 - 2N_8 = 6 \chi = 12\]

If there are heptagons present (in the case of the carbon nanopearls), this number of pentagons require changes. For each heptagon, an extra pentagon is required to close the structure\textsuperscript{[44]}. The more heptagons, the more pentagons (twice as many), which leads to an increase in the overall diameter of the sphere.

![Figure 2.16: a.) Hexagon ring carbon structure with zero curvature, b.) pentagon ring structure with curvature around $+60^\circ$, c.) heptagon ring structure with outward curvature around $-60^\circ$\textsuperscript{[44]}](image)

a.) hexagon ring  b.) pentagon ring  c.) heptagon ring
According to Wang et al., this growth process is ideal for all carbon nanospheres (regardless of the growth method).

As mentioned, carbon nanopearls can be grown using various methods. Some of these methods include: growth from glucose using hydrothermal conditions [3], non-catalytic chemical vapor deposition (CVD) preparation [4], de-oiled asphalt [5], direct pyrolysis of hydrocarbons [6], arc discharge and autoclave methods [47], and CVD growth of carbon nanopearls using Ni catalyst [7]. The chemical vapor deposition process has been mentioned earlier in section 2.2.3.1 when carbon nanotubes were discussed. A. Levesque et al., reported the use of CVD for carbon nanopearl synthesis. In their process, they used Ni catalyst 100 nm in size, a gas mixture of 20 % C₂H₂/ 80 % N₂ at a flow rate of 80:400 sccm (respectively), and a growth temperature of 700°C. As a result, the authors report CNPs with a size of 150 nm (fig. 2.17). Carbon nanopearls that have been grown using other methods have different sizes. For example, He et al., used the arc discharge method to obtain what they referred to as carbon balls [47]. In their setup, the anode was a carbon rod that contained both Fe and Ni, and the cathode was a graphite rod. They reported sphere sizes that were between 50-100 nm. Carbon spheres have also been grown by carbonization of acetone at 550°C, on Ni foil, in an autoclave [47]. These spheres were reported to be 4-5 μm (fig. 2.18).
Carbon nanopearls exhibit field emission properties that would be ideal for cathode materials\[9\]. The small radius of curvature (~75 nm), and the dangling bonds from the unclosed graphitic flakes, makes carbon nanopearls appealing for cathode materials. When compared to carbon nanotubes, carbon nanopearls are better for cathode materials as a result of there being no requirement for structure orientation. A. Levesque \textit{et al} reported field emission measurements of carbon nanopearls. Their data shows carbon nanopearls obtained currents up to 50 \(\mu\)A under continuous emission (see fig. 2.19).
for Levesque et al., field emission results)\cite{7}. Along with their field emission properties, recently there have been reports supporting evidence of carbon nanopearls as potential tribological coatings and lubricant additives\cite{9}. There has also been some research on carbon nanopearls as potential transporters of proteins, nucleic acids, and drug molecules in the nuclear membrane and across the cell membrane\cite{10}.

![Figure 2.19: Field emission data taken from carbon nanopearls\cite{7}.](image)

2.3 Difference Between Carbon Nanopearls and Other Carbon Structures

There are a few differences between carbon nanopearls and other carbon structures (such as graphene, buckyballs, carbon nanotubes and carbon nano-onions). These differences are found in structure and properties. Structure and property comparison of carbon nanopearls and other carbon structures can be found in table 2.1. Carbon nanopearls have a spherical structure, which consists of hexagonal sheets with
pentagonal and heptagonal rings (to enable bending of the structure). Like carbon nanopearls, carbon nano-onions are spherical. However, carbon nano-onions contain multiple “buckyball like” spheres. Their structure consists of pentagons and hexagons only. Carbon nano-onions are often referred to as multiple buckyballs. Carbon nanotubes have a cylindrical structure, consisting of single or multiple graphene sheets. Though the structures of carbon nanomaterials are different, graphene has been found to be the fundamental structure for all of these carbon structures. Comparing the properties, carbon nanopearls are different from the other carbon structures in table 2.1 due to their field emission and tribology capabilities. Carbon nanotubes are field emitters, however, they are restricted to emitting from the tip of the tube. Carbon nanopearls are not dimension restricted when used as field emitters.

<table>
<thead>
<tr>
<th>Table 2.1 Comparison of carbon structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Material</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>graphene</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>buckyballs ($C_{60}$)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>carbon nanotubes</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>carbon nano-onions</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>carbon nanopearls</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>
2.4 Summary of Carbon Structures

Carbon structures come in many forms. The structures that have been discussed in this proposal were the natural minerals, such as diamond and graphite, and the synthetic carbon materials: fullerenes, carbon nano-onions, carbon nanotubes and carbon nanopearls. These carbon structures share many commonalities and differences (see table 2.1). Fullerenes ($C_{60}$ to be specific), carbon nano-onions, and carbon nanopearls are similar in that they have spherical structures. They are all sp$^2$ hybridized carbon structures made up of graphitic sheets (carbon nano-onions and buckyballs), or graphitic flakes (carbon nanopearls). As mentioned in section 2.2.2, carbon nano-onions are basically carbon spheres with layers of fullerene shells wrapped inside one another. Carbon nanotubes are sp$^2$ hybridized, however, they are cylindrical structures that are made up of either one graphite sheet (SWCNTs) or multiple graphitic sheets (MWCNTs). Graphite is the fundamental backbone to the structure of the synthetic carbon structures mentioned in this paper. The synthetic structures that were discussed in this review share a lot of the same growth methods: arc discharge, laser ablation, and CVD. Research shows that different growth conditions are used to prepare each type of material (i.e., temperatures, carbon sources, and gases). Unlike graphite, and the synthetic carbon structures mentioned in this review, diamond is sp$^3$ hybridized. It is has high thermal conductivity and can be a great semiconductor. It is the hardest natural material known to man. Carbon nanotubes are the hardest synthetic material known to man, with hardness values comparable to diamond ($\sim 1$ TPa). Review of these carbon structures shows the commonality of field emission properties. Carbon nanotubes, buckyballs, and carbon nanopearls all show great potential for cold cathode materials as a result of their field
emission capability. Carbon nanopearls show the best potential for cold cathodes due to their radius of curvature, and lack of restraints on structure orientation (this is where carbon nanotubes suffer in field emission capability).

The following section will present background information of common catalysts used for synthesis of carbon materials. This will be followed by details of growth mechanisms for synthesis of carbon structures that use nickel catalyst.

2.5 Catalysts used for Synthesis of Carbon Structures

2.5.1 Iron

Iron (Fe) is one of the many widely used catalysts for synthesis of carbon structures. It is a transition metal with a body-centric cubic crystal structure (BCC)\cite{13}. Iron has a melting temperature of 1538°C and a density of 7.87g/cm$^{-3}$ (as a bulk material) as a result of the high bonding strength\cite{48}. The high melting temperature is one of the reasons why this transition metal is used as a catalyst in CVD synthesis of carbon structures. The catalyst can withstand the high temperatures that are involved in CVD. Like the other transition metals that will be mentioned in the following sections, Fe can break down hydrocarbons\cite{48}. This is why Fe is a great material for catalysis. Iron has a carbon solubility of 20.2 at % (bulk property at melting temperature). However, this solubility decreases with particle size- leading to carbon precipitation. When carbon is precipitated from the catalyst, carbon structures begin to form. This will be discussed further in section 2.6. The main disadvantage of this transition metal as a catalyst is the problem of oxidation. Iron forms an oxide at room temperature. Nevertheless, hydrocarbons release hydrogen atoms that reduce the oxide, allowing the Fe to perform
as a catalyst. The melting temperature, ability to decompose hydrocarbons, carbon solubility and low cost are the main reasons that this transition metal is an excellent catalyst for synthesis of carbon structures.

2.5.2 Cobalt

Another transition metal that has been used as a catalyst for synthesis of carbon structures is cobalt (Co). On the periodic table, cobalt has the atomic number 27 and can be found between iron and nickel\textsuperscript{[49]}. This ferromagnetic metal has both a face centered cubic (FCC) and hexagonal closed packed (HCP) structure. The melting temperature (bulk), slightly lower than iron, is 1495°C\textsuperscript{[48]}. Cobalt has a density of 8.85 g/cm\textsuperscript{3} (very close to nickel, which will be mentioned in the following section). Not only has Co proven to decompose hydrocarbon precursors, but the carbon solubility (13.9 at % at the melting temperature) has shown to be significant in the growth mechanisms underlying synthesis of carbon structures\textsuperscript{[48]}. One report has stated that cobalt catalysts have produced more ordered carbon structures than other transition metal catalysts\textsuperscript{[50]}. However, a conflicting report has stated that nickel results in the most “carbonaceous deposits”\textsuperscript{[51]}. The disadvantage of this metal catalyst is that it is very expensive compared to iron and nickel. Therefore, iron and nickel are often chosen as catalysts in synthesis of carbon nanostructures.

2.5.3 Nickel

The final catalyst that will be discussed is nickel (Ni). This silvery-white transition metal has a face centered cubic (FCC) structure, and has the atomic number 28 on the chemical elements table\textsuperscript{[49]}. The melting temperature of Ni is 1453°C, less than both Fe and Co. Nickel has a bulk density of 8.908g/cm\textsuperscript{3}. Similar to the previously
discussed metals, nickel has a high bonding strength as well. The carbon solubility of Ni is 10.7 at% for bulk material. Like iron and cobalt, nickel is ferromagnetic; this transition metal has shown evidence of decomposing hydrocarbon precursors as well. The disadvantage of nickel is that it oxidizes under certain conditions (e.g., when heated in air)[49]. However, nickel appears to be favored as a catalyst for carbon nanomaterial synthesis as opposed to iron and cobalt.

The following section will focus on growth mechanisms using nickel as a catalyst for synthesis of carbon nanotubes, carbon nano-onions and carbon nanopearls.

2.6 Growth Mechanism of Carbon Structures Grown Using Nickel Catalyst

2.6.1 Carbon nanotubes

Although a growth mechanism for carbon nanotubes hasn’t been established, literature shows that scientists agree on a very common proposed mechanism[52]. The common growth mechanism (applies to Ni, Co, and Fe) is the following: the hydrocarbon precursor decomposes into carbon and hydrogen products following contact with the metal nanoparticles (at elevated temperatures), the carbon dissolves into the metal catalyst, the nanoparticle becomes saturated with the carbon atoms until reaching the solubility limit, carbon precipitates outside of the nanoparticle, and finally the carbon forms a tubular network attached to the metal nanoparticle. The tubular structure can grow in two ways, top-down (or tip-growth) and top-up (also known as base-growth method)[52]. The top-down method is the following: after the metal nanoparticle has reached its carbon solubility limit, the carbon precipitates out of the bottom of the particle, and the tube grows downward-pushing the particle off the substrate (see fig. 2.20).
Figure 2.20: Top-down/tip-growth mechanism of carbon nanotubes on metal nanoparticle (Ni, Co, Fe)\(^{[52]}\).

The carbon nanotube continues to grow until the top of the metal catalyst is completely covered (by carbon atoms). The top-up method consists of the following: after the metal nanoparticle has reached its carbon solubility limit (just like in the top-down method), precipitation of the carbon out of the center of the top of the metal catalyst in a crystalline hemispherical dome occurs, followed by extension of the carbon dome in the upward direction in a tubular form, the growth continues as carbon deposits on the bottom of the metal, dissolves and diffuses upward, and finally the growth ends when the metal catalyst is completely covered with carbon atoms (see fig. 2.21 for top-up method)\(^{[52]}\).
Both the top-up and top-down growth mechanisms for carbon nanotubes have been the common proposed models for carbon nanotube growth. These models are used for all three transition metals that are used as a catalyst (Ni, Co, and Fe).

As mentioned in section 2.2.2, carbon nano-onions have a spherical shape. These carbon nano-onions have a different growth mechanism than carbon nanotubes. The growth mechanism of carbon nano-onions will be described in the following section.

### 2.6.2 Carbon nano-onions

A few growth mechanisms have been proposed for carbon nano-onions. All of the proposed mechanisms had different conditions (e.g., growth method, precursor, temperature). This section will focus on the growth mechanism explained for carbon nano-onions synthesized using CVD.

There are two growth mechanisms that have been proposed for carbon nano-onions synthesized using chemical vapor deposition: vapor solid (VS) mechanism and vapor liquid (VL) mechanism. These two mechanisms result in two different carbon nano-onions: a metal filled core (VS mechanism), and an empty core (VL
mechanism\textsuperscript{[53]}. The VS mechanism is the following: carbon vapor from the precursor is adsorbed by nickel nanoparticle, layers of graphite are formed around the surface of the nanoparticle, layers continue to form until the catalyst loses activity (see fig. 2.22)\textsuperscript{[53]}.

![Image of VS mechanism](image1.png)

Figure 2.22: VS mechanism for carbon nano-onion growth. Produces carbon nano-onions with metal core\textsuperscript{[53]}.

The VL mechanism for the carbon nano-onion with an empty core is similar to the VS mechanism. The difference is that the solid Ni nanoparticle becomes a liquid nanoparticle, and evaporates through defects present in the layers of graphite around the nickel particle. The melting temperature for nanoparticles is lower than the bulk material melting temperature (this is known as the Gibbs Thomson Effect, which will be explained in section 2.7). Therefore, the solid nickel nanoparticle melts and becomes a liquid particle, which then leads to evaporation through the graphitic layers. The model for the VL mechanism can be seen in figure 2.23.

![Image of VL mechanism](image2.png)

Figure 2.23: Vapor liquid mechanism for carbon nano-onion growth (no metal core)\textsuperscript{[53]}. 
2.6.3 Carbon nanopearls

There are quite a few growth mechanisms that explain carbon sphere growth. Like carbon nano-onions, the growth mechanism for carbon sphere growth is dependent on the growth conditions (e.g., growth method, precursor, and temperature). For carbon spheres that are solid (carbon nanopearls, CNPs), the growth mechanism has not been clearly defined. A.A. Deshmukh et al., mentions that solid carbon spheres are produced as a result of the catalyst “aiding the decomposition”, instead of “assisting with the polymerization reaction”[47]. This implies that the carbon is never adsorbed or absorbed by the nickel catalyst. Instead, the carbon sphere forms separate from the catalyst, and the sphere is formed by joining and aggregation of pentagonal, heptagonal and hexagonal structures (see section 2.2.4 for review of carbon nanopearl structure)[47]. Z.L. Wang and Z.C. Kang also propose that the carbon spheres grow with the same structure (pentagonal, heptagonal and hexagonal])[54]. However, the growth method Z.L. Wang et al use is mixed-valent oxide-catalytic carbonization (MVOCC), and instead of forming separate from the catalyst, the authors believe the carbon spheres grow on the catalyst and then detach[54].

For the carbon nanopearls synthesized in this dissertation, I propose another growth mechanism. This growth mechanism will be based on the results found in this research, and will be presented in the conclusion chapter of this dissertation. The Gibbs-Thomson effect and Kelvin effect will be discussed in the following sections.

2.7 Gibbs-Thomson Effect

Research has shown that as the particle size decreases, depression of the melting point occurs simultaneously. This is a result of the Gibbs-Thomson effect. According to
Yasushi Shibuta and Toshio Suzuki, the Gibbs-Thomson effect “is a depression of the equilibrium temperature at the solid-liquid interface with curvature during solidification” \[^{[55]}\]. The expression for the Gibbs-Thomson effect is the following:

\[
\Delta T = \frac{2T_m \sigma_{SL}}{\rho_s \Delta H} \frac{1}{r}
\]

Where \( r \) is the radius of the nanoparticle, \( \sigma_{SL} \) is the solid-liquid interfacial energy, \( \Delta H \) is the latent heat of melting, \( \rho_s \) is the number density of the solid phase, \( \Delta T \) is the melting point depression and \( T_m \) is the melting point of the bulk material\[^{[55]}\]. This expression will be used to calculate the theoretical melting temperature of the nickel nanoparticles used for CVD synthesis of carbon nanopearls, as part of the investigation of the nickel behavior.

**2.8 Kelvin Effect**

Liquid droplets of small radius and high curvature have a high vapor pressure when compared to the bulk liquid vapor pressure. The high curvature of the small droplet reduces the coordination number of the surface atoms, which leads to high vapor pressure\[^{[56]}\]. This is the Kelvin effect, the outcome of curvature on the vapor pressure of liquids\[^{[56]}\]. The equation for the Kelvin effect is the following:

\[
P = P_o \exp \left( \frac{2\gamma V}{RT_r} \right)
\]

where \( P \) and \( P_o \) are the particles vapor pressure and bulk vapor pressure, respectively. The surface tension is \( \gamma \), \( \bar{V} \) is the molar volume of the liquid, and \( R \) and \( T \) are the gas constant and the absolute temperature (respectively)\[^{[60]}\]. The radius, \( r \), is inversely proportional to the vapor pressure. The smaller the radius, the higher the vapor pressure.
It is believed that the nickel nanoparticles become a liquid, and then these spheres begin to evaporate as a result of the Kelvin effect. This will be studied and the results will be presented later in this dissertation.
3. RESEARCH OBJECTIVES

The objective of this research program was as follows:

To investigate the behavior of the nickel catalyst in chemical vapor deposition synthesis of carbon nanopearls.

This was done by the following: growth of carbon nanopearls using two different catalyst sizes (20 nm and 100 nm), carbon nanopearls were grown at various growth times to enable observation of change of chemical constituents over growth time (10 s, 30 s, 60 s, 90 s, 120 s, 300 s). Characterization of the change in Ni phases over growth time were conducted using X-ray diffraction and X-ray photoelectron spectroscopy. A question that was addressed is “does the nickel evaporate during chemical vapor deposition synthesis of carbon nanopearls”? This was addressed experimentally and theoretically. Two experiments were conducted to analyze the evaporation of nickel: thermal gravimetrical analysis on nickel (both the 20 nm and 100 nm), and measurement of the change in weight of nickel after heating to three different temperatures (300°C, 600°C, and 900°C). Theoretically, the Kelvin equation was used to analyze the change in vapor pressure of the Ni nanoparticles (for both sizes). An increase in vapor pressure lowers the temperature at which the atoms from the Ni nanoparticles begin to vaporize (evaporate). It was believed that the nickel melts during the CVD heat ramping. Therefore, differential
scanning calorimetry was performed on nickel to analyze the melting temperature. The Gibbs-Thomson equation was used to estimate the melting temperature and compared to the experimental values. Other characterization (such as TEM and Raman spectroscopy) were performed to observe the carbon nanopearls structure over growth time. A model for the growth of carbon nanopearls is presented in chapter 6 based on the results presented here.
4. EXPERIMENT METHODS

The following sections explain the procedures, experimental conditions, and characterization techniques used to investigate the behavior of the nickel in CVD synthesis of carbon nanopearls. The results from these experiments are presented in Chapter 5 of this dissertation.

4.1 Starting Material

There were two Ni sizes used in this research: 20 nm and 100 nm. The 20 nm Ni nanoparticles were obtained from Sun Innovation, and had 99.8 % purity (fig. 4.1). The 100 nm Ni nanoparticles were obtained from Alfa Aesar, with a 99.8 % purity as well (fig. 4.2). The amount of nickel used for each experiment was 0.02 g.

Figure 4.1: 20 nm Ni nanoparticles, from Sun Innovation, used for all experiments. The picture on the right is a transmission electron microscopy image of the 20 nm Ni nanoparticles.
Figure 4.2: 100 nm Ni nanoparticles, from Alfa Aesar, used in all experiments. The picture on the right is a transmission electron microscopy image of the 100 nm Ni nanoparticles.

4.2 Chemical Vapor Deposition Furnace

A Barnstead International, Model F21135 chemical vapor deposition (CVD) quartz tube furnace (with a tube diameter of 38.1 mm), was used for the synthesis of CNPs (see fig. 4.3). An 63.5 mm x 19.05 mm x 9.53 mm quartz boat was designed to place the nickel nanopowder in for CNPs synthesis (fig. 4.4).
Figure 4.3: CVD furnace.

Figure 4.4: 63.5 mm x 19.05 mm x 9.53 mm quartz boat.
4.3 Growth Process

The 63.5 mm x 19.05 mm x 9.53 mm quartz boat, containing the nickel nanopowders, was placed in the CVD furnace and set for a growth temperature of 850 °C for 2 minutes. The gases that were used during this process were acetylene (carbon precursor, purity grade of 99.6%) and argon (purity grade of 99.9999%). Levesque et al. reported using nitrogen in their growth process for carbon nanopearls\(^7\). Argon was used in this research due to gas availability (there were no differences in results, which will be explained in chapter 5). The argon continuously flowed through the quartz tube furnace while the heating was in process. The acetylene was turned on at 850 °C for the desired growth time (see growth time experiments in section 4.4), and then it was immediately shut off. The argon continuously flowed while the furnace cooled to room temperature (this enabled balanced pressure inside and outside the furnace). The flow rates of the acetylene and argon were 80:400 sccm, respectively. Following the growth of the carbon nanopearls, the sample was collected from the quartz boat and prepared for characterization.

4.4 Growth Time Experiments

Carbon nanopearls were grown at 850 °C for the following growth times: 10 sec, 30 sec, 60 sec, 90 sec, 120 sec, and 300 sec. Both catalyst sizes (20 nm and 100 nm) were grown three times for each growth time. This gave a total of 36 growth time experiments. The purpose of growing the samples three times for each growth time was to demonstrate reproducibility of the results.

4.5 Characterization Methods

The following characterization methods were used for this research, and will be defined in sections below: X-ray diffraction (XRD), X-ray photoelectron spectroscopy
Characterization of the constituents during growth of the CNPs was analyzed via XRD. Raman spectroscopy of the carbon nanopearls enabled structural and vibration analysis, and TEM rendered analysis of the internal structure of the CNPs via transmitted electrons. Weight loss versus temperature for the nickel was measured using TGA, and the melting temperature of the nickel nanoparticles was measured using DSC. X-ray photoelectron spectroscopy also enabled chemical composition analysis of the carbon nanopearls over growth time, however, this characterization tool only provided information from the surface of the material. These characterization instruments were useful to the objective of this research, which was to investigate the behavior of the Ni in CVD synthesis of CNPs. These characterization tools also enabled answers to the questions regarding the melting temperature and the fate of the nickel.

4.5.1 X-ray diffraction

X-ray diffraction was obtained using a Rigaku DMAX B horizontal diffractometer, in a symmetric theta-two theta reflective mode (Bragg-Brento geometry) (see fig. 4.5). The patterns were analyzed using the Joint Committee on Powder Diffraction Standards (JCPDS) data. The carbon nanopearl samples were dispersed onto a glass substrate that had double sided tape. The Cu K-alpha radiation was produced using a rotating anode generator at 40 kV and 150 mA with a diffracted beam monochromator. The data was then analyzed and compared to JCPDS diffraction files using MDI Jade 6.5 software.
4.5.2 X-ray photoelectron spectroscopy

XPS was obtained by placing the CNP s samples on double sided tape attached to a quartz substrate (see XPS system in fig. 4.6). The XPS spectra were acquired on a Perkin-Elmer Phi 5300 XPS system, equipped with a hemispherical energy analyzer and a non-monochromatic aluminum X-ray source with a nominal photon energy of 1486.6 eV. Survey spectra were acquired with 0.5 eV step size, a dwell time of 100 ms, and sweeping 50 times, for a total spectral acquisition time of 233 min. High resolution spectra were acquired with 0.1 eV step size, dwell time 100 ms, and 400 sweeps. The photoelectron take-off angle was 45 degrees and the x-ray illumination angle was 54.7 degrees relative to the acceptance window of the energy analyzer. Compositions were calculated using Casa XPS software, employing atomic sensitivity factors for X-ray sources at 54.7 degrees, after performing Shirley background subtraction. Chemical state determination was performed by fitting the observed spectra with component peaks having 70% Gaussian / 30% Lorentzian peak shapes.
Figure 4.6: X-ray photoelectron spectrometer.

4.5.3 Raman spectroscopy

Raman spectroscopy was performed on the CNPs utilizing an excitation wavelength of 532 nm, with a maximum power output of 0.01 mW (fig. 4.7). After XRD was taken on the CNPs samples, the same samples were used for Raman analysis (CNPs on glass substrate containing double sided tape). Scans were taken at a location on the sample within the range of 100 to 3000 cm$^{-1}$, at 10 % of the maximum output power, for 30 sec per scan.
4.5.4 Transmission electron microscopy

A LaB₆ Phillips TEM was used to characterize the structure of the carbon nanopearl samples (fig. 4.8). The samples were sonicated for 5-15 minutes (each sample separately) to prevent agglomeration. Following sonication, the sample was drop cast (using a pipette) onto a carbon coated Cu grid (200 mesh grid), followed by drying under a hood. After the sample dried, it was placed in the microscope for characterization. High magnifications were used to observe the structure of the carbon nanopearls for each different catalyst size.
4.5.5 Thermal gravimetric analysis

A TA Instruments’ Q500 TGA was used for thermal stability determination (see fig. 4.9). Approximately 10 mg of sample was placed in a platinum pan under a nitrogen atmosphere using the standard ceramic lined furnace. Following a room temperature isothermal stabilization for 10 minutes to allow N₂ to fully purge the sample, the dynamic scans were performed using a ramp rate of 10°C/minute to a final temperature of 1000°C.
4.5.6 Differential scanning calorimetry

A Netzsch DSC 404 F3 was used to analyze the melting temperatures of the Ni nanoparticles (see fig. 4.10). The particles were heated at 20 °C/min, to 800 °C at atmospheric pressure. The samples were heated in an Al₂O₃ crucible, with argon flowing at a rate of 50 mL/min.
4.6 Weight Loss Experiments

Along with the TGA analysis for weight loss measurements, 12 experiments were conducted to measure weight loss (see table 4.1). Both the 20 nm Ni and the 100 nm Ni were heated at 300 °C, 600 °C and 900 °C and then cooled down (no dwelling at temperature). The weight of the samples was measured before and after heating. Heating at three different temperatures enabled an estimate of the evaporation temperature of the Ni nanoparticles. This will be compared to the temperatures provided by TGA. The Kelvin effect will be used to analyze the change in the vapor pressure as the radius of the nanoparticle decreases (mentioned in section 2.8). If the vapor pressure is smaller than the vapor pressure for the bulk material, the nanoparticle evaporates at lower temperatures than the bulk material.
<table>
<thead>
<tr>
<th>Ni catalyst (nm)</th>
<th>Mass before heating 300 °C</th>
<th>Mass after heating 300 °C</th>
<th>Mass before heating 600 °C</th>
<th>Mass after heating 600 °C</th>
<th>Mass before heating 900 °C</th>
<th>Mass after heating 900 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 nm</td>
<td>2 samples</td>
<td>2 samples</td>
<td>2 samples</td>
<td>2 samples</td>
<td>2 samples</td>
<td>2 samples</td>
</tr>
<tr>
<td>100 nm</td>
<td>2 samples</td>
<td>2 samples</td>
<td>2 samples</td>
<td>2 samples</td>
<td>2 samples</td>
<td>2 samples</td>
</tr>
</tbody>
</table>
5. RESULTS

5.1 Chemical Constituents During Growth Time

The following results are from the growth time experiments conducted on the carbon nanopearls that were grown using 100 nm Ni nanoparticles and 20 nm Ni nanoparticles. The growth time experiments were conducted three times for both the 100 nm and 20 nm Ni nanoparticles to determine repeatability (see table 5.1 for growth experiment details). X-ray diffraction (XRD) was used to observe the change in the chemical constituents during growth time. The variation in the chemical composition of constituents and phases for each experiment was observed and compared in the summary of the XRD results.

<table>
<thead>
<tr>
<th>Catalyst Size (nm)</th>
<th>Growth Time (in seconds)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10 s</td>
</tr>
<tr>
<td>20 nm</td>
<td>3</td>
</tr>
<tr>
<td>100 nm</td>
<td>3</td>
</tr>
</tbody>
</table>

XRD was performed on the metallic Ni catalyst prior to carbon nanopearl growth, where the diffraction peak broadening for the 20 nm Ni nanoparticles is noticeable as compared to the 100 nm Ni nanoparticles (see fig. 5.1). Results for the CNPs grown in the first experiment, using the 100 nm Ni nanoparticles, are shown in figure 5.2. The graph shows four different crystalline phases present over the growth time experiments:
graphite, Ni$_3$C, NiO and Ni (the 3 curves at the bottom of fig. 5.2 are reference curves). At 10 sec (red curve) peak diffractions occur for NiO (101) and (012) at 2-theta angles of 37.2° and 43.2° in figure 5.2 (respectively). The same NiO peaks occur at 30 sec (blue curve) and 60 sec (green curve) of CNPs growth. For the 90 sec growth (purple curve), there were diffraction peaks for Ni$_3$C ((100), (002), (101) and (102)) and metallic Ni ((111) and (200)). The peaks for Ni$_3$C occurred at 2-theta angles of 39.1°, 41.6°, 44.6° and 58.4°. The peaks for metallic Ni were at 44.5° and 51.8° (the Ni peaks from the CNPs samples are identical to the Ni peaks for the as is Ni catalyst in fig. 5.1).

Figure 5.1: XRD analysis of Ni catalyst before CVD experiments. The 20 nm Ni has a larger peak as a result of the smaller size. Slight shifting in the peaks is due to sample placement in system.
Figure 5.2: XRD results of carbon nanopearl samples grown using 100 nm Ni, with
growth times of the following: 10 sec (top red curve), 30 sec (blue curve, 3rd from top),
60 sec (green curve, 4th from top), 90 sec (purple curve), 120 sec (grey curve) and 300
sec (black curve). The bottom three curves are reference curves.

From the graph (fig. 5.2), it appears as if the diffraction peaks for Ni may have occurred
as early as 30 sec (this can be seen in table 5.2, which lists the relative chemical
composition for the samples grown using the 100 nm Ni nanoparticles, for each
experiment). However, the peak for Ni is most intense at 90 sec growth. Also, NiO is still
apparent in the 90 sec growth curve, but it is not as intense as in the earlier growth times.
At the 120 sec growth (grey curve in fig. 5.2), it appears that NiO and Ni₃C have
disappeared completely. The two chemical constituents identified at 120 sec are graphite
and Ni. The graphite diffraction peak (002) exists at 26.6°. Both Ni and graphite
diffraction peaks appear at 300 sec growth time as well. Table 5.2 lists the chemical
composition at each growth time, for each of the crystalline phases that are shown in fig.
5.2. According to table 5.2, the sample goes from 100% NiO at 10 sec growth, to only 1.8% at 90 sec and finally 0 at 120 sec. As the NiO composition decreased the Ni and Ni$_3$C composition increased, reaching a maximum of 30.3% (Ni) and 67.9% (Ni$_3$C) at 90 sec. At 120 sec and 300 sec, there was 100% metallic Ni. Graphite had a quantitative measurement of 18.8% and 33% at 120 sec and 300 sec (respectively).
Table 5.2 Relative chemical composition, for each phase and constituent present in CNPs grown at various times. (values are in %)

<table>
<thead>
<tr>
<th>Growth time (sec)</th>
<th>Experiments</th>
<th>NiO</th>
<th>Ni</th>
<th>Ni3C</th>
<th>Gr</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>Exp1</td>
<td>100.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>Exp2</td>
<td>0.0</td>
<td>97.6</td>
<td>2.4</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>Exp3</td>
<td>74.1</td>
<td>47.5</td>
<td>21.5</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>Aver</td>
<td>58.0</td>
<td>48.4</td>
<td>8.0</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>StDev</td>
<td>51.9</td>
<td>48.8</td>
<td>11.8</td>
<td>2.0</td>
</tr>
<tr>
<td>30</td>
<td>Exp1</td>
<td>89.7</td>
<td>7.7</td>
<td>2.6</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>Exp2</td>
<td>0.0</td>
<td>99.8</td>
<td>0.2</td>
<td>6.9</td>
</tr>
<tr>
<td></td>
<td>Exp3</td>
<td>0.0</td>
<td>98.8</td>
<td>0.5</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>Aver</td>
<td>29.9</td>
<td>68.8</td>
<td>1.1</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>StDev</td>
<td>51.8</td>
<td>52.9</td>
<td>1.3</td>
<td>3.5</td>
</tr>
<tr>
<td>60</td>
<td>Exp1</td>
<td>94.9</td>
<td>2.2</td>
<td>2.9</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>Exp2</td>
<td>0.0</td>
<td>100.0</td>
<td>0.0</td>
<td>8.4</td>
</tr>
<tr>
<td></td>
<td>Exp3</td>
<td>0.0</td>
<td>99.2</td>
<td>0.2</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>Aver</td>
<td>31.6</td>
<td>67.1</td>
<td>1.0</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>StDev</td>
<td>54.8</td>
<td>56.2</td>
<td>1.6</td>
<td>4.3</td>
</tr>
<tr>
<td>90</td>
<td>Exp1</td>
<td>1.8</td>
<td>30.3</td>
<td>67.9</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>Exp2</td>
<td>0.0</td>
<td>100.0</td>
<td>0.0</td>
<td>20.2</td>
</tr>
<tr>
<td></td>
<td>Exp3</td>
<td>0.0</td>
<td>99.8</td>
<td>0.0</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>Aver</td>
<td>0.6</td>
<td>76.7</td>
<td>22.6</td>
<td>7.8</td>
</tr>
<tr>
<td></td>
<td>StDev</td>
<td>1.0</td>
<td>40.2</td>
<td>39.2</td>
<td>10.9</td>
</tr>
<tr>
<td>120</td>
<td>Exp1</td>
<td>0.0</td>
<td>100.0</td>
<td>0.0</td>
<td>18.8</td>
</tr>
<tr>
<td></td>
<td>Exp2</td>
<td>0.0</td>
<td>100.0</td>
<td>0.0</td>
<td>14.2</td>
</tr>
<tr>
<td></td>
<td>Exp3</td>
<td>0.0</td>
<td>99.0</td>
<td>0.0</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>Aver</td>
<td>0.0</td>
<td>99.7</td>
<td>0.0</td>
<td>11.6</td>
</tr>
<tr>
<td></td>
<td>StDev</td>
<td>0.0</td>
<td>0.6</td>
<td>0.0</td>
<td>8.8</td>
</tr>
<tr>
<td>300</td>
<td>Exp1</td>
<td>0.0</td>
<td>100.0</td>
<td>0.0</td>
<td>33.0</td>
</tr>
<tr>
<td></td>
<td>Exp2</td>
<td>0.0</td>
<td>100.0</td>
<td>0.0</td>
<td>77.2</td>
</tr>
<tr>
<td></td>
<td>Exp3</td>
<td>0.0</td>
<td>97.9</td>
<td>0.0</td>
<td>32.5</td>
</tr>
<tr>
<td></td>
<td>Aver</td>
<td>0.0</td>
<td>99.3</td>
<td>0.0</td>
<td>47.6</td>
</tr>
<tr>
<td></td>
<td>StDev</td>
<td>0.0</td>
<td>1.2</td>
<td>0.0</td>
<td>25.7</td>
</tr>
</tbody>
</table>

54
Transmission electron microscopy on the carbon nanopearl samples grown using the 100 nm Ni catalyst is shown in figure 5.3. Selected area diffraction (SAD) was performed on some of the samples as well (via TEM). At 10 sec, there was no structure, and the SAD diffraction spots form rings that correspond to the following planes: (111), (200) and (220). These planes confirm that the diffraction pattern is that of NiO. As growth time increased, the sample became slightly spherical at 90 sec (this is when Ni$_3$C and Ni increased in quantity). At 120 sec and 300 sec, carbon nanopearls were formed. SAD patterns at 120 sec and 300 sec were similar to what has been published in the literature regarding carbon nanopearls[11].

The average size of the carbon nanopearls at 120 sec was 282.12 nm (with an error of 9.02 nm). At 300 sec, the average size of the carbon nanopearls was 346.69 nm (with an error of 5.76 nm). This means longer growth time produced larger carbon nanopearls. In summary, the material starts off as NiO when grown for 10 sec. As the growth time increased, NiO reduced and metallic Ni and Ni$_3$C appear. Nickel carbide decomposes, leaving only metallic nickel and the increase of graphite at the longer growth times.
Figure 5.3: TEM and SAD images of samples grown at various growth times using 100 nm Ni nanoparticles. Left to right, from the top: a) NiO (10 sec), b) SAD pattern with diffraction planes (111), (200) and (220) confirming NiO at 10 sec, c) 90 sec, d) carbon nanopearls at 120 sec, e) carbon nanoparl at 300 sec, f) carbon nanopearls at 300 sec, higher magnification, g) halo ring from SAD of CNPs grown for 5 min, showing amorphous carbon.

The results for carbon nanopearls grown using the 20 nm Ni catalyst, in the first experiment, are presented in figure 5.4 and table 5.3. Just like for the 100 nm samples, there are diffraction peaks for NiO (confirmed by the planes (111), (200) and (220)) at 10 sec for the 20 nm samples (red curve in fig. 5.4). Quantitatively, the XRD measured 100 % NiO at 10 sec (see Table 5.3). At 30 sec (blue curve in fig. 5.4), the NiO diffraction peaks are still present, however, the Ni$_3$C diffraction peaks and metallic Ni diffraction peaks are also identified at this growth time. Table 5.3 shows the relative chemical compositions for Ni$_3$C and Ni at 30 sec was ~15.3 % and ~1.1 % (respectively). It appears that the 20 nm sample at 30 sec has more Ni$_3$C present than the 100 nm sample, and less Ni. At 60 sec (green curve, fig. 5.4 for 20 nm samples) the graph shows diffraction peaks for metallic nickel, and a slight peak for graphite. Table 5.3 shows that the chemical composition for the 20 nm sample at 60 sec was ~96.7 % Ni, ~1.6%
graphite, ~1.2 % NiO and ~2.1 % Ni$_3$C. When comparing the 20 nm and 100 nm samples it appears that graphite develops sooner (60 sec) for 20 nm than it does for 100 nm (which had 0 % graphite at 60 sec). The graph for 90 sec (purple curve in fig. 5.4 for 20 nm) has diffraction peaks for Ni and graphite. It appears that for the 20 nm samples, the NiO disappears sooner (0 % NiO at 90 sec according to quantitative data in table 5.3) than the 100 nm samples. Also, there is less Ni$_3$C at 90 sec for the 20 nm samples than there is for the 100 nm samples, and more graphite present at 90 sec for the 20 nm samples than there is for the 100 nm samples. At 120 sec and 300 sec, the graphs for the 20 nm samples are identical, with metallic Ni and graphite diffraction peaks (fig. 5.4). There is a noticeable increase in the graphite peak when the growth time goes from 120 sec to 300 sec. However, quantitative measurements show a bit more graphite present at 120 sec (~18.2 %) than at 300 sec (~17.7%) for the 20 nm samples. In summary, use of smaller Ni nanoparticles results in quicker formation of graphite.
Figure 5.4: XRD analysis of CNPs grown using 20 nm Ni nanoparticles. Bottom three curves are reference curves.

TEM and SAD of the 20 nm CNPs samples were performed as well. Figure 5.5 shows images taken at different growth times. Just like with the 100 nm CNPs samples, there was no structure at 10 sec, and the SAD pattern confirmed there was NiO. As growth time increased, features seen in the TEM became spherical. Finally, at 120 sec and 300 sec, there were carbon nanopearls. The average size of the carbon nanopearls at 120 sec was 302.70 nm (+/- 7.54 nm), and the average size at 300 sec was 292.98 nm (+/- 18.46 nm). The average CNPs size for the 20 nm samples was smaller than the average CNPs size for the 100 nm samples at 300 sec. However, the 20 nm CNPs samples had an average size slightly larger than 100 nm CNPs sample at 120 sec.
In summary of the results for the CNPs grown using the 20 nm Ni nanoparticles in the first experiment, the sample starts off as NiO. As growth time increases the NiO reduces, Ni increases, graphite increases and Ni$_3$C increases then hits zero. The CNPs grown using the 20 nm catalyst react sooner than the CNPs grown using the 100 nm catalyst. The fast reaction of the 20 nm samples is a result of the larger surface area (per volume). Reactivity of a nanoparticle is enhanced as the surface area increases$^{[57]}$. The surface area for 20 mg of Ni nanoparticles with a diameter of 20 nm is 5 times larger than the surface area for 20 mg of Ni nanoparticles with a diameter of 100 nm. This explains why the samples grown using the 20 nm Ni react faster than the 100 nm Ni.
<table>
<thead>
<tr>
<th>Growth time (sec)</th>
<th>Experiments</th>
<th>NiO</th>
<th>Ni</th>
<th>Ni3C</th>
<th>Gr</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>Exp1</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Exp2</td>
<td>0.4</td>
<td>98.4</td>
<td>1.2</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>Exp3</td>
<td>12.1</td>
<td>25.7</td>
<td>62.2</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>Aver</td>
<td>37.5</td>
<td>41.4</td>
<td>21.1</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>StDev</td>
<td>54.5</td>
<td>51.1</td>
<td>35.6</td>
<td>0.2</td>
</tr>
<tr>
<td>30</td>
<td>Exp1</td>
<td>83.6</td>
<td>1.3</td>
<td>15.1</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>Exp2</td>
<td>0.0</td>
<td>98.8</td>
<td>1.0</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>Exp3</td>
<td>0.0</td>
<td>98.0</td>
<td>1.4</td>
<td>7.9</td>
</tr>
<tr>
<td></td>
<td>Aver</td>
<td>27.9</td>
<td>66.0</td>
<td>5.8</td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td>StDev</td>
<td>48.3</td>
<td>56.1</td>
<td>8.0</td>
<td>4.0</td>
</tr>
<tr>
<td>60</td>
<td>Exp1</td>
<td>1.2</td>
<td>96.7</td>
<td>2.1</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>Exp2</td>
<td>0.3</td>
<td>99.2</td>
<td>0.3</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>Exp3</td>
<td>0.0</td>
<td>99.3</td>
<td>0.0</td>
<td>13.6</td>
</tr>
<tr>
<td></td>
<td>Aver</td>
<td>0.5</td>
<td>98.4</td>
<td>0.8</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td>StDev</td>
<td>0.6</td>
<td>1.5</td>
<td>1.1</td>
<td>6.7</td>
</tr>
<tr>
<td>90</td>
<td>Exp1</td>
<td>0.0</td>
<td>70.5</td>
<td>29.5</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td>Exp2</td>
<td>0.0</td>
<td>99.8</td>
<td>0.0</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>Exp3</td>
<td>0.0</td>
<td>99.5</td>
<td>0.0</td>
<td>11.4</td>
</tr>
<tr>
<td></td>
<td>Aver</td>
<td>0.0</td>
<td>89.9</td>
<td>9.8</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td>StDev</td>
<td>0.0</td>
<td>16.8</td>
<td>17.0</td>
<td>4.4</td>
</tr>
<tr>
<td>120</td>
<td>Exp1</td>
<td>0.0</td>
<td>100.0</td>
<td>0.0</td>
<td>18.2</td>
</tr>
<tr>
<td></td>
<td>Exp2</td>
<td>0.0</td>
<td>99.9</td>
<td>0.0</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>Exp3</td>
<td>0.0</td>
<td>99.3</td>
<td>0.0</td>
<td>13.1</td>
</tr>
<tr>
<td></td>
<td>Aver</td>
<td>0.0</td>
<td>99.7</td>
<td>0.0</td>
<td>11.0</td>
</tr>
<tr>
<td></td>
<td>StDev</td>
<td>0.0</td>
<td>0.4</td>
<td>0.0</td>
<td>8.4</td>
</tr>
<tr>
<td>300</td>
<td>Exp1</td>
<td>0.0</td>
<td>100.0</td>
<td>0.0</td>
<td>17.7</td>
</tr>
<tr>
<td></td>
<td>Exp2</td>
<td>0.0</td>
<td>97.9</td>
<td>0.0</td>
<td>32.5</td>
</tr>
<tr>
<td></td>
<td>Exp3</td>
<td>0.0</td>
<td>97.2</td>
<td>0.0</td>
<td>41.9</td>
</tr>
<tr>
<td></td>
<td>Aver</td>
<td>0.0</td>
<td>98.4</td>
<td>0.0</td>
<td>30.7</td>
</tr>
<tr>
<td></td>
<td>StDev</td>
<td>0.0</td>
<td>1.5</td>
<td>0.0</td>
<td>12.2</td>
</tr>
</tbody>
</table>
Figure 5.5: Left to right, from the top: a) NiO (20 nm sample at 10 sec), b) SAD pattern, c) 90 sec, d) carbon nanopearls (120 sec), e) carbon nanopearls (300 sec), f) carbon nanopearls at higher magnification showing fridges of carbon flakes at edge, g) SAD of 300 sec CNPs showing amorphous carbon halo.

The experiments were repeated 2 more times (for each catalyst size) to ensure the results were reproducible. The XRD results are shown in figure 5.6-5.10, and quantitative data was also recorded and presented in table 5.2 and 5.3. The results in figure 5.6 (100 nm CNP samples) and figure 5.7 (20 nm CNPs samples) are the results from the 2nd experiment. Both figures show graphite and metallic Ni diffraction peaks at every growth time. There were no NiO diffraction peaks for both the 100 nm and 20 nm CNPs samples presented in figure 5.6 and 5.7 (unlike the XRD results for the CNPs samples in fig. 5.2 and fig. 5.4). There were very small diffraction peaks for Ni$_3$C as early as 10 sec for both the 100 nm and 20 nm CNPs samples. However, these peaks are very small and don’t appear as growth time increase. The graphite peak intensity (and quantity) increased with growth time for both catalyst size (see tables 5.2 and 5.3 for quantitative measurements).
Figure 5.6: XRD analysis of CNPs grown using 100 nm Ni nanoparticles.
Figure 5.7: XRD analysis of CNPs grown at various growth times using 20 nm Ni nanoparticles.

The XRD results from for the CNPs grown in the 3rd experiment are presented in figure 5.8 and 5.9. These figures show different results in comparison to the data presented in the 2nd experiment (fig. 5.6 and 5.7). The results in figure 5.8 and 5.9 show diffraction peaks for NiO at 10 sec (similar to the data in the 1st experiment, fig. 5.2 and 5.4). There are diffraction peaks for Ni$_3$C at 10 sec and 30 sec for both the 100 nm and 20 nm CNPs samples presented in figure 5.8 and 5.9. The graphite diffraction peaks occurred at every growth time (for both catalyst size), and increased in intensity (and quantity) with time (see tables 5.2 and 5.3 for quantitative measurements). The results in figure 5.9 show that the 20 nm CNPs react sooner than the 100 nm CNPs samples. This
again is supported by the literature that states the larger the surface area, the faster the reaction of the nanoparticle.

Figure 5.8: XRD analysis of CNPs grown at various growth times using 100 nm Ni nanoparticles.
Figure 5.9: XRD analysis of CNPs grown at various growth times using 20 nm Ni nanoparticles.

In summary, the CNPs were grown at various growth times and the experiments were conducted three times to check reproducibility in results. The Ni catalyst developed different phases over carbon nanopearl growth time-starting from a metallic and oxidized state, transitioning to Ni$_3$C phase, and finally a graphite and metallic Ni phase at the longer growth times. The NiO phase was present in the earlier growth times for the first and 3$^{rd}$ experiment, but not during the 2$^{nd}$ experiment. It is not understood why there was no NiO in any of the samples during the 2$^{nd}$ experiment. However, switching off the argon gas between experiments could have resulted in a change of purity. If the argon purity was lower than 99.9999 % during experiments 1 and 3, impurities (e.g., oxygen) could have been present during the growth leading to oxidation at higher temperatures.
Figure 5.10 and 5.11 show the change in NiO composition as growth time progresses for each experiment. Based on the results from each experiment conducted, it appears that the CNPs growth process doesn’t begin until that NiO layer has been reduced. The metastable Ni$_3$C phase was reproduced each time, but at different growth times and compositions. Finally, graphite and metallic Ni diffraction peaks were reproduced for every growth time experiment. After observing all of the results, it appears that the 20 nm samples react at a faster rate than the 100 nm samples. As mentioned previously, literature states that the larger the surface area, the faster the chemical reaction$^{[57]}$. This supports the XRD results for the CNPs grown using 20 nm Ni nanoparticles. Also, the 20 nm catalyst produced CNPs with a smaller size than the CNPs produced with the 100 nm catalyst. The next section continues to discuss the chemical constituents as growth time changes. However, the analysis was taken using XPS. This data is based on the surface of the samples, and will be compared to the XRD analysis.
Figure 5.10: Variation of the NiO phase for each CNPs growth experiment using the 100 nm Ni catalyst, at various growth times. The error bars represent variation (standard deviation) of the NiO phase composition from the average composition.
Figure 5.11: Variation of the NiO phase between for each CNPs growth experiment using the 20 nm Ni catalyst, at various growth times. The error bars represent variation (standard deviation) of the NiO phase composition from the average composition.

5.2 Surface Chemical Analysis (XPS)

Surface chemical analysis was performed using a XPS with a non-monochromatic Al-Kα radiation. XPS measurements were taken on carbon nanopearl samples grown using the 20 nm nickel. As before, samples were grown at various growth times (10 sec, 30 sec, 60 sec, 90 sec, 120 sec, and 300 sec). High resolution XPS scans were performed on all of the samples except for 10 sec (due to lack of sample available for characterization). As the growth time increased above 30 seconds, carbon deposition on the catalyst surface had prevented photoelectron escape from underlying nickel surface, preventing identification and analysis of the nickel related peaks. Therefore, high
resolution XPS scans were performed for Ni 2p region for 30 seconds, and for other growth times only C 1s detailed scans were performed. The Ni 2p region spectra components were fitted using duplet Gaussian-Lorentzian curves, where the 2p ½ peak fits for each of the shown component were constrained by the following conditions: peak area was 50% of the 2p 3/2 peaks, and 2p ½ peak central position was +18.5 eV from 2p 3/2.

The first sample scanned was the CNPs grown for 30sec. There are two spectra for this sample, Ni and C. The results for the Ni and C spectra can be found in figure 5.12 and 5.13 (respectively). For the Ni 2p region, the spectra shows peaks for the following components in figure 5.12 (binding energy, BE, in electron volts- eV): Ni 2p 3/2 (850.8 eV) and Ni 2p 1/2 (869.1 eV), NiO 2p 3/2 (854.7 eV) and NiO 2p 1/2 (873.0 eV), Ni$_2$O$_3$ 2p 3/2 (861.3 eV and 879.6 eV), and potentially NiCO$_3$ 2p 1/2 (856.9 eV and 875.2 eV). The spectra was fitted for the compound NiCO$_3$ based on the weak shoulder at 856.9 eV, which is very close to the NiO 2p 3/2 peak (854.7 eV). Literature shows that NiCO$_3$ peaks were present at 855.5 eV, during methane deposition over Ni particles (see fig. 5.13 small graph for referenced peaks)\cite{58}. There are other reports that found NiCO$_3$ at 854.7 eV. The presence of NiCO$_3$ could have been a result of the early stages of the deposition of carbon onto the catalyst. As the growth time increased, carbon deposition on the surface began to increase making it difficult to identify the nickel related peaks.
Figure 5.12: XPS data on carbon nanopearls grown using 20 nm Ni nanoparticles for 30 sec. Spectra of Ni 2p curve fitting. Inset graph is from referenced literature\textsuperscript{[58]}.

The spectra for C 1s was fitted for the following components: NiC\textsubscript{x} (carbide measured at 281.0 eV), carbon (284.5 eV), and COH (288.4eV). The NiC\textsubscript{x} and carbon peaks were both reported in the deposition of methane on Ni particles (see fig. 5.13 graph inset)\textsuperscript{[58]}. Table 5.4 lists the quantitative measurements obtained by XPS of the carbon nanopearl sample grown for 30 sec (1% Si not shown in the table).
Figure 5.13: XPS spectra of carbon peaks at 30 sec of carbon nanopearls grown using 20 nm Ni nanoparticles. The small graph is spectra from results found in the literature\cite{58}.

As growth time increased, the NiC\textsubscript{x} curve grew in intensity (see fig. 5.14 and 5.15). The carbide reached a maximum intensity at 90 sec (fig. 5.15) and had shifted to a central location of 282 eV, indicating a formation of a well developed Ni\textsubscript{3}C phase. The carbon concentration increased with growth time, and the nickel concentration decreased. Table

<table>
<thead>
<tr>
<th>Peak</th>
<th>Quantity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>29</td>
</tr>
<tr>
<td>C</td>
<td>34</td>
</tr>
<tr>
<td>O</td>
<td>36</td>
</tr>
</tbody>
</table>

As growth time increased, the NiC\textsubscript{x} curve grew in intensity (see fig. 5.14 and 5.15). The carbide reached a maximum intensity at 90 sec (fig. 5.15) and had shifted to a central location of 282 eV, indicating a formation of a well developed Ni\textsubscript{3}C phase. The carbon concentration increased with growth time, and the nickel concentration decreased. Table
5.5 lists the concentration for Ni, C, and O over growth time (nitrogen concentration of 1-2 % not included in table). After 90 sec, the carbon peak began to increase in both intensity and quantity (see fig. 5.16 for 120 sec growth). The carbon peak began to change shape from broad and symmetrical at early growth times to narrow and asymmetrical at 300 sec growth time (see fig. 5.17 for 300 sec XPS spectra). This indicated the structural evolution of carbon from amorphous to graphite. Further indications that the carbon peak was a graphite peak was the pi shake-up peaks that occurred around 291 eV\textsuperscript{[59]}. The pi shake ups result when the pi-\pi bond is excited. Excitation of the pi-\pi bond is a result of emission of the photoelectrons from the 284.5 energy\textsuperscript{[59]}. This shake up of the pi bond results in a peak at 291 eV, with an intensity of only 5-10% of the graphite peak\textsuperscript{[60]}. The pi shake up is common when there is graphitic material (see inset in fig. 5.17).
Figure 5.14: XPS spectra of CNPs sample grown using 20 nm Ni nanoparticles for 60 sec. NiCₓ peak is increasing.
Figure 5.15: XPS spectra of CNPs sample grown using 20 nm Ni nanoparticles for 90 sec. NiCₓ peak at maximum intensity.
Figure 5.16: XPS spectra of CNPs sample grown using 20 nm Ni nanoparticles for 120 sec. NiCₓ peak has gotten weaker, and C peak intensity has grown.
In summary, XPS allowed chemical analysis of the surface of the carbon nanopearl samples as growth time increased. Results showed that there were a few nickel oxide phases at 30 sec, and possibly a NiCO₃ phase. The nickel oxide components were due to the presence of oxygen contaminants in the argon gas that was flown through the
CVD furnace. The presence of nickel oxide was also a result of the samples being exposed to the laboratory air during transfer from furnace to characterization equipment. The NiCO₃ compound could be due to the adsorption of carbon at 30 sec. As time increased, the nickel and nickel compound peaks could no longer be detected due to the carbon deposition. Simultaneously, as growth time increased, the carbide peak on the C spectrum increased. This is similar to the XRD data where the nickel carbide peak appears at 30 sec, and its intensity increases with growth time. The carbide peak, in the XPS results, reaches its maximum intensity at 90 sec. After 90 sec growth, the 284.6 eV carbon peak (and concentration) increases, and by 300 sec it was graphite (the carbide peak is no longer present). This data was similar to the XRD data. For the XRD, graphite concentration increases with growth, and the carbide (being a metastable phase) decomposes by 120 sec. The next section will discuss the results from structure analysis of the carbon nanopearls grown, using 20 and 100 nm Ni nanoparticles at the various growth times.

5.3 Structure Analysis (Raman)

Raman spectroscopy was performed on all of the carbon nanopearl samples that were grown at various growth times. This technique enabled observation of the disorder in the CNPs structure. The main features that were observed were the D band, G band and 2D band. The D band, 1350 cm⁻¹, identifies disorder in sp² hybridized carbon material. The G band occurs around 1580 cm⁻¹, and occurs when there is stretching of the sp² carbon bond. Materials such as carbon nanotubes, carbon nanopearls and graphene have a G band. Lastly, the 2D band (also referred to as G') has been reported to occur in the range of 2500-2800 cm⁻¹. Like the G band, the 2D band also represents
graphitic sp² hybridized materials. The 2D band is a very common feature for observing layer thickness in graphene materials (though, it is not commonly observed when analyzing carbon spheres). This band can also be used to determine how ordered or disordered the stacking of the ABAB structures are in graphitic materials[64]. These three features (D, G and 2D band) are very commonly observed when analyzing Raman spectra of carbon nanomaterials. The ID/IG ratio was calculated from the intensities of the D and G band. This ratio determined how ordered the structure was, with a lower number indicating order and less defects. In addition, the I2D/IG ratio was observed with some of the samples.

The spectra for CNPs grown using the 100 nm and 20 nm Ni are shown in figure 5.18 and 5.19 (respectively). For the CNPs grown using the 100 nm, data could only be retrieved from samples grown for 90 sec, 120 sec and 300 sec. These samples had enough carbon so that it could be detected by Raman. According to the spectra in figure 5.18, it looks like the G band was very narrow, and had a higher intensity than the D band for all samples. The 2D band was higher than the D band, but lower than the G band at each growth time. Curve fitting was performed using Gaussian-Lorentzian curves. The data from the curve fitting allowed calculations of the ID/IG. The ID/IG helped analyze the spectra, and get a better idea of the structure for the samples. This data is shown in table 5.6. It appeared that for the CNPs grown using the 100 nm Ni at 90 sec, the ID/IG ratio was very low, ~0.24, which indicates the sample had an ordered-graphitic structure (with minimum defects). As the growth time increased to 120 sec, the structure became very disordered, with a ID/IG of ~1.16. At 300 sec, the ID/IG decreased to ~0.44, indicating this sample had more order and less defects than the sample grown for 120 sec (but more
disorder and defects than the 90 sec sample). The $I_{2D}/I_G$ for the CNPs grown using 100 nm Ni (not shown in table) indicated that there was disorder in the stacking of the graphene structure for the 90 sec sample (~0.69), and this disorder increased with growth time (~1.09 at 300 sec). The average $I_{2D}/I_G$ for the CNPs grown using 100 nm Ni, for 90 sec, 120 sec and 300 sec was 0.61 (+/- 0.48)

Figure 5.18: Raman spectra of CNPs samples grown using the 100 nm at the growth times: 90 sec, 120 sec, and 300 sec.
<table>
<thead>
<tr>
<th></th>
<th>( I_D/I_G )</th>
<th>( I_{2D}/I_G )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>100 nm CNPs growth</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>time samples</td>
<td></td>
<td></td>
</tr>
<tr>
<td>90 sec</td>
<td>0.24</td>
<td>0.69</td>
</tr>
<tr>
<td>120 sec</td>
<td>1.16</td>
<td>0.80</td>
</tr>
<tr>
<td>300 sec</td>
<td>0.44</td>
<td>1.09</td>
</tr>
<tr>
<td><strong>20 nm CNPs growth</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>time samples</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60 sec</td>
<td>1.10</td>
<td>0.82</td>
</tr>
<tr>
<td>90 sec</td>
<td>0.43</td>
<td>0.98</td>
</tr>
<tr>
<td>120 sec</td>
<td>0.32</td>
<td>0.98</td>
</tr>
<tr>
<td>300 sec</td>
<td>0.30</td>
<td>0.88</td>
</tr>
</tbody>
</table>
The results for the CNPs grown using the 20 nm Ni are shown in figure 5.19. As a result of the 20 nm Ni catalyst reacting sooner than the 100 nm Ni (i.e., there was carbon present at earlier growth times), there was Raman spectra for the growth times of 60 sec, 90 sec, 120 sec and 300 sec. Figure 5.19 shows that at 60 sec, the D and G band were about the same height. As the growth time increased, the G band intensity grew- and the D band slightly decreased. At 300 sec, both the G and D band intensity had decreased. The 2D band followed the same intensity trend as the G band. The inset spectra in figure 5.19 was published in the literature by A. Levesque and V.T. Binh\[7\]. Their Raman results on carbon nanopearls showed a very broad D peak at 1350 cm\(^{-1}\), and a broad G peak at 1590 cm\(^{-1}\). The D band also
had a higher intensity than the G band in the A. Levesque et al paper. Their results indicated that they had very disordered graphitic planes within their carbon nanopearls. When comparing the Raman results reported by A. Levesque et al to the Raman results in figure 5.18 and 5.19, it appears that the CNPs grown using both catalyst size had more order and less defects. Table 5.6 shows the $I_D/I_G$ for the CNPs grown using the 20 nm Ni. At 60 sec, the disorder was very high ($I_D/I_G \sim 1.09$). According to XRD and XPS, there was carbide present at this growth time, which could explain the disorder. As growth time increased, the disorder decreased, with an $I_D/I_G \sim 0.30$ at 300 sec. There was more disorder present at 300 sec for the 100 nm Ni sample than there was for the 20 nm Ni sample at 300 sec. The average $I_D/I_G$ for the CNPs grown using the 20 nm Ni at growth times 60 sec- 300 sec was 0.54 (±0.38). When analyzing the $I_{2D}/I_G$ (not shown in table 5.10), the disorder was high and approached 1.0 as the growth time increased. This meant that like the 100 nm samples, the stacking of the structure for the 20 nm samples was disordered.

As mentioned in section 5.1, the CNPs growth time experiments were conducted three times. As a result, Raman analysis was performed on two more CNPs growth time experiments. The data was used to calculate the $I_D/I_G$ for each of the samples. An average for each sample set was taken and placed in table 5.7. For the second experiment, the average $I_D/I_G$ for the CNPs grown using the 100 nm and 20 nm Ni was 0.31 (± 0.14) and 0.29 (±0.05), respectively. The 100 nm CNPs samples in the third growth time experiment had an average $I_D/I_G$ of $\sim 0.29$ (± 0.06) as well. This means that the structure was ordered with minimum defects. The $I_D/I_G$ ratio slightly increased for the 20 nm CNPs samples in the third experiment (0.44 ± 0.24), hinting to more disorder in the samples for this set. The $I_{2D}/I_G$ (not presented in table 5.7) showed much more disorder in the graphitic structure for the second
and third experiment, for both the 100 nm and 20 nm CNPs samples. The ratio increased with each growth time experiment, meaning the stacking order of the structure was very misaligned.

<table>
<thead>
<tr>
<th>Table 5.7 Average $I_D/I_G$ for CNPs grown using 100 nm and 20 nm Ni in the 2nd and 3rd experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment 2</td>
</tr>
<tr>
<td>100 nm</td>
</tr>
<tr>
<td>20 nm</td>
</tr>
<tr>
<td>Experiment 3</td>
</tr>
<tr>
<td>100 nm</td>
</tr>
<tr>
<td>20 nm</td>
</tr>
</tbody>
</table>

Raman analysis enabled observation of changes in the structure as growth time changed. Figure 5.20 shows the average $I_D/I_G$ for all three carbon nanopearl experiments grown using the 100 nm. The average $I_D/I_G$ of all three growth time experiments grown using the 100 nm is $0.40 \pm 0.18$ (not shown in fig. 5.20). The CNPs grown using the 100 nm Ni started off with minimum defects and disorder in the structure, but there was a big increase at the growth time of 120 sec, followed by decrease in the disorder. The 20 nm CNPs samples, in the first experiment, had a high disorder ratio at earlier growth times, but the ratio decreased with growth indicating a more ordered structure. Figure 5.21 shows the average $I_D/I_G$ for all three carbon nanopearl experiments grown using the 20 nm catalyst. The average $I_D/I_G$ of all three growth time experiments grown using the 20 nm is $0.42 \pm 0.13$ (not shown in fig. 5.21). As mentioned previously, the samples had an ordered structure with minimum defects (e.g., intrinsic defects). The 20 nm CNPs
samples in the third experiment had an increase in disorder, but still showed less disorder than the CNPs grown in the first experiment. The next section discusses the melting temperature of the nickel nanoparticles by DSC measurements, and the Gibbs-Thomson model.

Figure 5.20: Average I_D/I_G for each CNPs experiment grown using the 100 nm Ni, at various growth times.
5.4 Melting of Nickel

So far, the chemical constituents and structure of the carbon nanopearls as functions of increasing growth time have been discussed. These next two sections will address the question (that was mentioned in chapter 3) of whether the Ni catalyst evaporates during synthesis of carbon nanopearls. In order to address this question, both melting temperature and evaporation temperature were measured experimentally and theoretically. This section will discuss the results from the melting temperature experiments, followed by the evaporation temperature measurements in section 5.5.

Differential scanning calorimetry is a technique that measures the heat flow and temperatures related to the materials physical/chemical transition as a function of
Both quantitative and qualitative measurements can be taken using DSC. The physical and chemical transitions that can be observed are endothermic (e.g., melting) and exothermic (e.g., crystallization). The material is heated to a maximum temperature (800 °C for this experiment) at a constant rate (20 °C/min in this study). As the material is heated, the heat flow is measured as temperature (and/or time) increases. A plot using the measured heat flow is made and the different transitions in the material are observed. These transitions can be identified using referenced DSC data on the material. For this research, a differential scanning calorimeter was used to measure the phase transitions of the Ni nanoparticles (both 20 nm and 100 nm). For the nickel nanoparticles, the goal was to find the endothermic transition for melting. However, only the melting temperature for the 20 nm Ni nanoparticles was observed (see fig. 5.22). For the 100 nm Ni nanoparticles, there were no transition peaks indicating melting (see fig. 5.23). In figure 5.22, there is a local minimum at 366.6 °C. This minima peak represents the melting temperature for the 20 nm Ni. The onset of melting, ~345.3 °C, was extrapolated from the curve. Generally, a good DSC melting curve would have a flat baseline and a symmetric endothermic peak, indicating that the material is pure, and the size of the nanoparticles is uniform. However, this result appears to have a melting endothermic peak at 366°C superimposed on a broad exothermic peak from approximately 100-500 °C. This broad exothermic peak from 100-500 °C is a result of impurities (e.g., oxidation) and variation in the nanoparticle size. Oxidation has been known to occur with Ni nanoparticles that have been heated in air. However, these samples were heated in nitrogen which should have prevented oxidation. This result indicates that the nitrogen feed contained some air contamination, although this does not affect the melting point result.
Figure 5.22: DSC measurements of 20 nm Ni nanoparticles (as is). Results show melting temperature of 366.6 °C.
Figure 5.23: DSC measurements of 100 nm Ni nanoparticles (as is). Results indicate oxidation occurred as nanoparticles were heated. There is a small dip in the curve around 350 °C, which may indicate a small portion of the sample melted.

The melting temperature extrapolated for the 20 nm Ni nanoparticles is lower than the bulk melting temperature of Ni ($T_{\text{m,bulk}} = 1453 ^\circ\text{C}$). This results in a melting point depression of 1086 °C. Section 2.7 mentioned how the Gibbs-Thomson effect says the smaller the radius, the larger the melting point depression. The melting temperature analyzed for the 20 nm Ni supports that argument. The melting temperature for the 100 nm Ni nanoparticles, however, wasn’t observed in the curve in figure 5.23. There was a small dip in the curve around 350 °C, which may indicate a small portion of the sample melting. However, this small dip is not the melting temperature. Instead, there was a broad exothermic peak- indicating oxidation. This exothermic peak was followed by a decrease in the curve. Following the exothermic peak, there is a decrease in the oxidation...
rate\cite{67}. As a result, the melting temperature could not be analyzed from the DSC data due to the nanoparticles oxidizing.

DSC measurements were performed twice for repeatability, and the average melting temperature for the 20 nm Ni was 366.4 °C ± 0.4 °C (average onset of melting was 345 °C ± 0.4 °C). The 100 nm nickel nanoparticles had the same behavior as before and oxidized while heating (the small dip around 350 °C did not occur during the second DSC scan). There have been DSC results published on the melting temperatures of Ni nanoparticles in the range of 10 nm to 100 nm (with an average size of 30 nm)\cite{68}. The literature reports melting temperatures for Ni particles, in the size range of 10 nm to 100 nm, of 300 °C and 500 °C\cite{68}. Their measurements are lower than the bulk melting temperature for nickel, and close to the results for the 20 nm Ni nanoparticles in this research. It was also reported in the literature that heavy oxidation occurred after 300 °C for the Ni nanoparticles. This is similar to the results that occurred with the particles in this research as well.

5.4.1 Gibbs-Thomson calculation

As mentioned in section 2.7, the Gibbs-Thomson effect states that the radius of the particle is inversely proportional to the melting point depression. Using the equation for the Gibbs-Thomson effect (see section 2.7), the melting point depression was calculated. The parameters used were: \( T_m = 1453 \ ^\circ C \)\cite{52}, \( \sigma_{sl} = 0.23 \ J/m^2 \)\cite{69}, \( r = 10 \text{ nm and } 50 \text{ nm}, \Delta H = 297 \text{ kJ/kg} \)\cite{70} and \( \rho_s = 8.90 \text{ g/cm}^3 \)\cite{13}. The calculation can be seen below:

\[
\Delta T = 2 \left( \frac{1453 \ ^\circ C \times 0.23 \ J/m^2}{8.90 \text{ g/cm}^3 \times 297 \text{ kJ/kg}} \right) \frac{1}{10 \text{ nm or } 50 \text{ nm}}
\]
ΔT_{10nm} = 25.29 °C and ΔT_{50nm} = 5.06 °C

According to the Gibbs-Thomson effect, the melting point depression for the nickel nanoparticle that has a 20 nm diameter (10 nm radius) is 25.29 °C. A melting point depression of 25.29 °C gives a melting temperature of $T_{20nm} = T_{m,bulk} - 25.29 °C = 1453 °C - 25.29 °C = 1427.71 °C$. This theoretical melting temperature is not even close to the melting temperature determined for the 20 nm Ni nanoparticles using DSC (351 °C). There is a difference of 1076.71 °C between the experimental value and the theoretical value. The melting point depression for the 100 nm nickel nanoparticle (50 nm radius) according to the Gibbs-Thomson effect was 5.06 °C. The experimental results for the 100 nm Ni nanoparticle could not be determined due to the sample oxidizing. It is unclear why there is an extremely large difference between the melting point depression found in the experiments and the melting point depression determined using the Gibbs-Thomson formula. Zhiming Wang reported a huge difference between the melting point depression found both experimentally and using the Gibbs-Thomson theory for their nanomaterial[71]. According to Wang, the experimental melting point reduction for their nanomaterial was greater than the Gibbs-Thomson calculations. Wang believes that the environment influences the melting temperature of the nanomaterial[71]. This could be the reason for the difference in the experimental and calculated melting point depression in this study. The argon that is flown during the DSC measurements may have aided in depressing the melting temperature of the Ni nanoparticles. Homma et al., reported an unexplained reduction in melting temperature for their nanoparticles when heated in argon, and an even lower melting temperature when heated in methane[72]. Wang and Homma et al., results support the DSC results for the melting temperature of the 20 nm Ni
nanoparticles. The Gibbs-Thomson theory does not take into account the surrounding environment. Therefore, based on the large difference between the experimental and theoretical value for the 20 nm Ni nanoparticle, it is likely that the Gibbs-Thomson effect is more of a guideline for calculating the melting point depression of the nanoparticles used in this research.

The next section will discuss the results from experiments conducted to determine if the Ni nanoparticles evaporated during heating to 850 °C for CNPs synthesis. The Kelvin effect was used to numerically determine if the Ni nanoparticles evaporate when heated.

5.5 Evaporation of Nickel

Results from the DSC show that the nickel (20 nm) melts at a lower temperature than the bulk melting temperature. As a result, the samples were tested to see if they evaporate following the melting stage. As mentioned in section 4.6, Nickel nanoparticles (both 20 nm and 100 nm) were heated at 300 °C, 600 °C and 900 °C (see table 4.1). The weight was measured both before and after heating. This experiment was conducted twice for each sample and the weight was measured using a balance scale (see table 5.8). To account for the amount of sample that may have been lost during collection from quartz boat, the measured amount of each sample is an approximation. All samples began with 20 mg. After 300 °C, the average weight for the 20 nm and 100 nm Ni was 17.9 mg (± 0.1 mg) and 19.2 mg (± 0.0), respectively. As temperature increased, the average weight for both samples was a little more than the starting mass (22.1 mg ± 0.2 mg for 20 nm Ni, and 22.3 mg ± 0. for 100 nm Ni). At the final heating temperature (900 °C), the average weight was 18.3 mg ± 0.3 mg for the 20 nm and 19.7 mg ± 0.2 mg for the 100
nm Ni nanoparticle. The DSC results show that there was oxidation of the nanoparticles as heating occurred. The color of the samples changed from the initial smoke grey (as is the color of the Ni nanoparticles) to a green color at 600 and 900 °C. As a result, these measurements didn’t reveal any signs of evaporation due to oxidation.

<table>
<thead>
<tr>
<th>Ni catalyst (nm)</th>
<th>Before heating to 300 °C</th>
<th>After heating to 300 °C</th>
<th>Before heating to 600 °C</th>
<th>After heating to 600 °C</th>
<th>Before heating to 900 °C</th>
<th>After heating to 900 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 nm</td>
<td>20.0 mg</td>
<td>17.9 mg</td>
<td>20.0 mg</td>
<td>21.9 mg</td>
<td>20.0 mg</td>
<td>18.3 mg</td>
</tr>
<tr>
<td>100 nm</td>
<td>20.0 mg</td>
<td>19.2 mg</td>
<td>20.0 mg</td>
<td>22.4 mg</td>
<td>20.0 mg</td>
<td>19.7 mg</td>
</tr>
</tbody>
</table>

Thermal gravimetric analysis (TGA) measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere\textsuperscript{[73]}. TGA samples were heated (at a constant rate) to a maximum temperature (1000 °C was the maximum temperature of the instrument) at which the sample mass has stabilized. Stabilization of the sample’s mass indicated that all chemical reactions had ceased\textsuperscript{[74]}. Thermal gravimetric analysis can be used to observe the composition of the sample constituents, and weight loss/gain as a result of oxidation, decomposition or dehydration. For the purposes of this research, TGA was performed on both the 20 nm and 100 nm Ni nanoparticles for weight loss measurements. Weight loss at a certain temperature can help to identify when the nanoparticle transforms to the gas state (i.e., evaporation). Each sample (10 mg of both 20 nm and 100 nm Ni nanoparticles) was heated to 1000 °C at a rate of 10 °C/min. The weight percentage vs. the temperature
increase was plotted for both Ni nanoparticle samples. Figure 5.24 shows that the 20 nm Ni nanoparticles had a weight loss of 1.45 % up to 400.35 °C (shown by the decreasing of the weight percent line from the starting position of 100 %), followed by a weight gain of 1.12 % up until 900.77 °C (shown by an increase of the weight percent line). The total weight loss for the 20 nm Ni nanoparticles was 0.33 %. This small weight loss has been reported to be a result of absorption of residues such as water and carbon dioxide when the sample was exposed to air\textsuperscript{[75]}. As the temperature increased, above 400.35 °C, the sample showed weight gain, indicating oxidation of the nickel particles. The DSC results showed evidence of the 20 nm Ni nanoparticles oxidizing as well (this was indicated by the broad, asymmetric shape of the curve before the melting peak in fig. 5.22). This analysis was conducted twice, and the average weight loss for the 20 nm Ni particles was 0.35 % (± 0.03 %), with the weight loss and gain occurring at the same temperatures.

Figure 5.25 shows the TGA results for the 100 nm Ni nanoparticles. The results show that the 100 nm Ni had a weight loss of 0.79 % up until 400.12 °C, followed by additional weight loss of 0.35 % up until 900.86 °C, for a total weight loss of 1.14 % from the starting weight of 10 mg. Like the 20 nm Ni particles, this weight loss can be attributed to absorption of residues such as water and carbon dioxide when the sample was exposed to air. The average weight loss for the 100 nm Ni particles was 0.57 % ± 0.81 (there was a weight gain from 400 °C to 900 °C the second time the TGA analysis was performed, a result of the material oxidizing). The DSC results for the 100 nm Ni particles shows a very broad exothermic peak, indicating the material oxidized (fig. 5.23). This supports the results found during the TGA analysis of the 100 nm Ni particles.
Figure 5.24: TGA of 20 nm Ni nanoparticles. Weight loss of 1.45 % up until 400.35 °C, then gains 1.12 % up until 900.77 °C. The total weight loss for this sample was 0.33 % from the starting weight of 10 mg.
Figure 5.25: TGA of 100 nm Ni nanoparticles. Weight loss of 0.79 % up until 400.12 °C, then loses another 0.35 % up until 900.86 °C. Total weight loss for this sample was 1.14 % from starting weight of 10 mg.

As a result of the Ni nanoparticles oxidizing, weight loss resulting from evaporation of particles could not be observed from the TGA results.

5.5.1 Kelvin effect

As mentioned in section 2.8, the Kelvin Effect states that the radius of the nanoparticle is inversely proportional to the vapor pressure. The smaller the radius, the higher the vapor pressure, meaning the particles are likely to evaporate at temperatures lower than the bulk evaporation temperature. This theory does not give a temperature for evaporation. However, one can assume that if $P > P_o$, then the particles will evaporate at a temperature lower than the bulk evaporation temperature. If $P < P_o$, then the particles will not evaporate at a lower temperature than the bulk. The vapor pressure for the 20 nm
Ni and 100 nm Ni nanoparticles was calculated using equation 2.6 in section 2.8. The following parameters were used for the calculation of the vapor pressure: $P_o = 237 \text{ Pa}^{[76]}$, $\gamma = 1.78 \text{ N/m}^{[77]}$, $\overline{V} = 6.59 \times 10^{-6} \text{ m}^3^{[76]}$, $T = 1726.15 \text{ K}$, $R = 8.3145 \text{ N-m}$, and $r = 10 \text{ nm}$ or 50 nm. For the 20 nm Ni nanoparticles, the calculated vapor pressure ($P_{20nm}$) was 279.09 Pa. The calculated vapor pressure for the 100 nm Ni nanoparticles ($P_{100nm}$) was 244.88 Pa. Comparing the theoretical values to the vapor pressure for bulk nickel, $P_{20nm} > P_o$ and $P_{100nm} > P_o$. Though the calculated vapor pressure for the nanoparticles was higher than the vapor pressure of bulk nickel, there wasn’t much of a difference (42.09 Pa between $P_{20nm}$ and $P_o$, and 7.88 Pa between $P_{100nm}$ and $P_o$). The higher vapor pressure for both the 100 nm and 20 nm particles indicate that the nanoparticles evaporate at a lower temperature, but it does not identify the temperature. Also, the results predict that the 20 nm Ni particles evaporate at a lower temperature than the 100 nm Ni particles.

The Kelvin Effect has been used in the literature to calculate the vapor pressure of nanoparticles. A. Moisala and A. Nasibulin used the Kelvin effect to calculate the vapor pressures for metal nanoparticles$^{[48]}$. From their results, Moisala et al constructed a graph showing the relation between nanoparticle size and vapor pressure at the melting temperature (see fig. 5.26). Figure 5.26 shows that the vapor pressure begins to increase at sizes below 10 nm for Ni. Although the Kelvin effect helps to relate size to vapor pressure, this theory does not incorporate time. It is believed that the time has an effect on the evaporation of the nanoparticle as well. The longer a nanoparticle is held at a temperature, the possibility of the particle evaporating increases. Therefore, the Kelvin effect is a guideline to determining the evaporation of nanoparticles.
Figure 5.26: Moisala et al results from vapor pressure calculations using the Kelvin effect\textsuperscript{[48]}.
6. DISCUSSION

The objective of this research was to investigate the behavior of the Ni catalyst during synthesis of carbon nanopearls. Carbon nanopearls were grown on both 20 nm and 100 nm Ni nanoparticles, at growth times of 10 sec, 30 sec, 60 sec, 120 sec and 300 sec. Results showed that the Ni reacted during the heating process, creating NiO at short growth times (10 sec-60 sec). The oxide was a result of the oxygen contaminants present in the Ar during CNPs synthesis. XRD and XPS revealed the following chemical phases as growth time increased: NiO, Ni$_2$O$_3$, Ni$_3$C, Ni, CO and C (both amorphous and graphite). XRD showed that as NiO reduced, Ni$_3$C increased. However, Ni$_3$C (being a metastable phase) decomposed leaving Ni and graphite at 120 sec and 300 sec. The graphite peak increased as growth time increased, and was most intense at 300 sec. Results from XRD also showed that the 20 nm Ni samples reacted faster than the 100 nm Ni. This is due to the 20 nm Ni nanoparticles having a surface area that was 5 times larger than the 100 nm Ni nanoparticles. XPS showed that as growth time increased, the C peak increased- going from amorphous to graphite at 300 sec (indicated by pi shake up bonds). XPS results showed Ni at 30 sec, but as the growth time increased carbon deposition prevented any detection of nickel. Images taken by the TEM and SAD confirmed that the material at the shortest growth time of 10 sec was NiO. At the longest growth times of 120 and 300 sec, the carbon nanopearls had grown (with a size increase
from 120 to 300 sec). The Ni$_3$C phase was not observed using TEM (future work will involve using a high-resolution microscope to try to observe the Ni$_3$C phase). TEM also revealed that there was a difference in the size of the CNPs grown using the 20 nm and 100 nm Ni catalyst. However, TEM showed that there was no catalyst present in the carbon sphere. Therefore, Ni that was observed by XRD was a result of the nickel that had segregated from the CNPs during synthesis, and agglomerated with other Ni particles.

The Raman spectra enabled comparison of the $I_D/I_G$ ratio as growth time increased for both the 20 nm and the 100 nm Ni. It was found that as the growth time increased, the $I_D/I_G$ value decreased, indicating an ordered graphite structure with minor defects. The Raman spectra also showed that the CNPs grown using the 100 nm Ni particles were more ordered than the CNPs grown using the 20 nm Ni particles.

A question that was addressed in this research was whether the Ni catalyst evaporates during synthesis of carbon nanopearls. This was addressed by analyzing both the melting temperature and vapor pressure of the Ni nanoparticles. The results from the DSC showed that both the 20 nm and 100 nm Ni nanoparticles reacted (oxidized) during heating. However, there was a phase transition identified as the melting peak for the 20 nm Ni particles. This melting peak occurred at an average temperature 366.4 °C for the 20 nm particles. The melting temperature for the 20 nm Ni particles, when compared to the bulk melting temperature, was a difference of 1086 °C. Results in the literature support this experimental melting temperature\cite{71}. A melting temperature for the 100 nm Ni particles could not be identified using DSC due to the particles completely oxidizing. Nevertheless, literature states that Ni particles in the size range of 10 nm to 100 nm have
a melting temperature around 300 °C and 500 °C\textsuperscript{[71]}. The Gibbs-Thomson theory says that the radius of the nanoparticle is inversely proportional to the melting point depression\textsuperscript{[59]}. Using this theory, the melting point depression was calculated and compared to the results found experimentally for the melting temperature. Results from the Gibbs-Thomson equation were $\Delta T_{10 \text{ nm}} = 25.29 \, ^\circ\text{C}$ (20 nm Ni nanoparticles) and $\Delta T_{50 \text{ nm}} = 5 \, ^\circ\text{C}$ (100 nm Ni nanoparticles). These theoretical values for the melting point depression meant that the melting temperature for the 20 nm Ni particles should have been 1427.71 °C and 1448 °C. The Gibbs-Thomson results were not close to the experimental results, as well as the results reported in the literature. As previously stated, the Gibbs-Thomson theory does not take into account the influence of the environment. Therefore, it was concluded that the Gibbs-Thomson theory was a guideline to determining the melting point of the nanoparticles.

The nickel nanoparticles (both 20 and 100 nm) were heated at 300 °C, 600 °C and 900 °C. Following each heating experiment, the nanoparticles were weighed to track weight loss (two samples for each heating time). The average weight for each sample (after heating at the temperatures) showed there was no significant weight loss. This was due to the Ni nanoparticles oxidizing during heating. The TGA results showed a small percent of weight loss (1-2 %) for both the 20 and 100 nm Ni particles before reacting (oxidizing). The small percentage of weight loss was due to water molecules that were absorbed when the sample was exposed to air. Reaction of the Ni nanoparticles caused weight gain in the TGA results (which explains why there wasn’t weight loss during heating experiments). Using the Kelvin theory, the vapor pressure was calculated and compared to the vapor pressure of the bulk material. The vapor pressure for both the 20
nm and 100 nm Ni nanoparticles was higher than the bulk vapor pressure (indicating the particles would evaporate at a lower temperature than the bulk). Though calculations from the Kelvin effect suggest that the Ni nanoparticles evaporate during the heating for CNPs synthesis (and that the 20 nm Ni particles evaporate easier than the 100 nm Ni particles), experimentally there is no evidence of the Ni nanoparticles evaporating.

In section 2.6.3 of this dissertation, the growth mechanism of carbon spheres reported in the literature was discussed. Based off the results found in this research, the following model for carbon nanopearl growth was proposed. Like carbon nano-onions that form by the VL mechanism (mentioned in section 2.6.2), the solid nickel particle melts and becomes a liquid particle (due to Gibbs-Thomson effect). The difference in the growth mechanism for the carbon nanopearls is the following: carbon atoms from the precursor are absorbed by the nickel catalyst and dissolved, followed by segregation of carbon atoms out of the liquid nickel particle. During carbon segregation, a metastable carbide phase (Ni$_3$C) forms. The carbide decomposes, and the nickel segregates through the defects of the graphite layers (see fig. 6.1), and agglomerates with other Ni particles. The carbon nanopearl continues to grow getting larger with time. There is no hollow core remaining in carbon nanopearls. This is a result of the carbon atoms dissolving in the liquid nickel particle until the particle has reached its solubility limit, followed by simultaneous segregation of both the carbon and nickel. This growth mechanism is another theory to explain how CNP are formed based on the results in this research, and the vapor liquid model proposed for carbon nano-onions that was mentioned in section 2.6.2$^{[53]}$. 

103
Figure 6.1: Carbon nanopearl growth model.
7. CONCLUSION

In these studies, the behavior of the Ni catalyst (both 20 nm and 100 nm) during carbon nanopearl growth was observed and reported. Prior to the use of CNPs as lubricants for tribological coatings or cathodes for field emission, the fundamental understanding of the Ni catalyst behavior is important. This research revealed that the Ni catalyst developed different phases over carbon nanopearl growth time – starting from metallic and oxidized state, transitioning to Ni$_3$C phase via a potential NiCO$_3$ intermediate step, then commencing the growth of CNPs, which the dissolution of the metastable Ni$_3$C phase and segregation of metallic nickel outside CNPs. The decrease of the catalyst size from 100 nm to 20 nm had considerably accelerated these processes, which had occurred with about twice as fast. The smaller catalyst size resulted in CNPs particles size decrease, which was reduced from about 350 nm to about 300 nm. This allows the conclusion that the catalyst size reduction has a considerable impact on the CNPs nucleation time and growth kinetics. Based off the results from this research, a growth model was proposed for the nickel catalyst evolution and carbon nanopearl nucleation and growth. The model enabled understanding of how the CNPs are formed during CVD synthesis, and how the nickel nanoparticle segregates from the CNPs during growth- leaving a solid carbon nanopearl. As a result, there are no limitations (that are related to the Ni catalyst) on carbon nanopearls use as cathodes for field emission or lubricants for tribology applications.
8. FUTURE STUDIES

Due to unavailability during these studies, high resolution TEM could not be performed on the carbon nanopearl samples. High resolution TEM would enable observation of the wavy structure of the carbon nanopearls, as well as chemical mapping. The chemical mapping would help to identify the Ni$_3$C phase. In addition to high resolution TEM imaging, longer growth time experiments (15 min to an hour) will be conducted. Longer growth times will be conducted to determine when the growth of the CNPs is terminated. Also, it is believed that the longer the growth time, the potential for Ni evaporation can occur. A purification method will be looked at to remove residual Ni nanoparticles as well. All excess Ni must be removed before being used as cathodes or in coatings for tribology use.
REFERENCE LIST


