

**Synthesis and Characterisation of Carbon Nanotube
Reinforced Hydroxyapatite Ceramics
for Biomedical Applications**

Catherine Sheree Kealley

**This thesis is presented for the Degree of
Doctor of Philosophy
of
University of Technology, Sydney**

March 2006

CERTIFICATE OF AUTHORSHIP/ORIGINALITY

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

Signature of Candidate

Production Note:
Signature removed prior to publication.

ABSTRACT

Reinforcement of nano-materials is important in many industrial processes, including the strengthening of biomedical implants for medical applications (for example artificial hip replacements). Human bone is mainly composed of collagen and hydroxyapatite (HAp) nanocrystals. HAp has been produced synthetically, with a structure and chemical composition almost identical to the HAp in human bone. When implanted, this synthetic material is accepted by the body. However, it has poor mechanical properties, making it unreliable for implant applications. The aim of this research is to combine biocompatible HAp with another biocompatible compound (carbon) to form a composite material with improved physical properties, including density, and strength.

The pure HAp was chemically synthesised using a precipitation reaction between calcium nitrate and diammonium hydrogenphosphate. The precipitate was centrifuged, washed and dried. After drying, the powder was heat-treated at 650 °C for 4 hours, and then hot isostatically pressed (HIP), at 100 MPa, 900 °C, in argon gas. Carbon nanotubes (CNTs) were chosen to reinforce the HAp based on their extreme flexibility and strength. Two production methods of incorporating CNT material (between 2 wt% and 10 wt% CNTs) into the HAp have been investigated: chemical precipitation reinforcement and physical reinforcement.

Full electron microscopy and diffraction characterisations of the pure and composite materials have been completed. The HIP process forms a dense pellet, with no voids between the CNT material and the HAp matrix. All CNTs imaged in the TEM had minimal degradation to the CNTs, with no visible change in the appearance. Unfortunately, the as supplied CNT material contained pockets of graphite which were non-uniformly distributed through the HAp matrix. Hence, the mixture was not homogeneous, and the CNTs were not bonding directly with the HAp. Neutron diffraction characterisation confirms that the crystal structure of the HAp was not affected by the CNT inclusion. Neutron diffraction patterns collected before and after sintering show that the CNTs must be heated in an inert atmosphere or a vacuum to prevent the CNT material from oxidising. TEM confirms no obvious visual damage to

the CNTs in the material. Neutron diffraction data have enabled the positions of the hydroxide bonds to be determined. Small-angle-neutron scattering showed that the surface morphology was rough. The CNT material dominated the neutron scattering results in the composite samples, which minimised the information obtained from the HAp matrix.

A range of physical properties of the pure HAp and the composite samples were measured. These included the density, porosity, surface area, hardness, fracture toughness, and Young's modulus. Two complementary techniques have been employed to measure the hardness; the Vickers microhardness and the Berkovich nanoindentation techniques. The density of the HIP samples of all of the materials was greater than ~94% of the theoretical density, with pure HAp materials as high as ~99%. The hardness values for the material measured by micro-indentation were quite high – either equal to or greater than the literature values. Unfortunately, this resulted in a lower fracture toughness, which was not improved by the addition of the CNTs. It is possible that, if the graphite phase were removed from the material, the fracture toughness could improve. Current CNT production methods do not allow full removal of the graphite.

Optical micrographs from the Vickers indentation tests of the composites show varying stages of lateral crack patterns formed, suggesting plastic deformation below the surface. This was consistent throughout all samples. The results from nanoindentation of the bulk material showed that, overall, the samples with the CNT material had a lower Young's modulus than the pure HAp samples (for both the laboratory synthesised and the commercial material). The microhardness and nanoindentation work showed that all of the samples were influenced by an indentation size effect, where the hardness decreased with increasing load.

Further work for increased fracture toughness in these composites requires the production of a pure CNT material (with no graphite impurity) for incorporation with the HAp. It is possible that, without the graphite impurity to bind the CNTs, they will spread more homogeneously throughout the HAp matrix, and bond along the CNT length. No pure CNT material was commercially available at the time of submission of this thesis.

ACKNOWLEDGEMENTS

First and foremost I would like to thank my supervisors Professor Arie van Riessen (Curtin), Dr. Margaret Elcombe (ANSTO), and Associate Professor Besim Ben-Nissan (UTS) for all their invaluable help and guidance throughout the course of my PhD. They have been a source of constant support and encouragement.

A large thanks goes to Dr. Bruno Latella (ANSTO), for the extensive time and expertise he provided in the physical property testing work. I would like to thank Dr John Bartlett, Dr Chris Howard, Mark Blackford, Gordon Thorogood, David Cassidy, Sam Moricca, Tina Eddowes, and Elizabeth Drabarek, at the Institute of Materials and Engineering Science, ANSTO, for making me feel so welcome, and for their shared specialised knowledge in their respective fields. Thanks also to Dr. Andrew Studer, Dr. Jamie Schulz, Dr. Elliot Gilbert and Dr. Robert Knott from the Bragg Institute, ANSTO, for their expertise in neutron diffraction and neutron scattering.

I would like to express my gratitude to Dr. Rob Hart, Dr. Nigel Kirby, Dr Matthew Rowles, Karsten Winter, Drew Sheppard and Glen Lawson from Curtin University of Technology for all the time and assistance they gave. Thanks also to Dr Richard Wuhrer, and Katie McBean at the University of Technology, Sydney, for the microscopy assistance, and Kanthi Lewis for her friendship and support.

I would like to gratefully acknowledge the funding that I received in the form of an APA Scholarship from Curtin University of Technology, a University of Technology, Sydney Doctoral Scholarship, and a Post-Graduate Research Award from the Australian Institute of Nuclear Science and Engineering. The synchrotron diffraction work was supported by the Australian Synchrotron Research Program, which is funded by the Commonwealth of Australia under the Major National Research Facilities Program. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Contract No. W-31-109-Eng-38.

On a personal note, I would like to thank my family and friends for all their support and encouragement throughout the years. I would especially like to thank Damien for his unending patience, time, effort, energy, understanding and support.

TABLE OF CONTENTS

ABSTRACT	i
ACKNOWLEDGEMENTS	iii
LIST OF FIGURES	viii
LIST OF TABLES	xv
1.0 INTRODUCTION	1
1.1 Background	1
1.2 Significance	2
1.3 Objective of Study	2
1.4 Research Plan	3
2.0 LITERATURE REVIEW	4
2.1 The Structure of Bone Tissue	4
2.1.2 <i>The Matrix of Bone</i>	6
2.1.3 <i>Compact and Spongy Bone Tissue</i>	8
2.1.4 <i>Structure of Human Hip Joint</i>	9
2.2 Calcium Phosphate Bioceramics	9
2.2.1 <i>Properties of Bioceramics</i>	10
2.2.2 <i>Similarity to Bone</i>	11
2.2.3 <i>Porosity</i>	11
2.2.4 <i>Bioactivity</i>	12
2.2.5 <i>Osteoconductive and Osteoinductive Properties</i>	12
2.2.6 <i>Applications of HAp Bioceramic material</i>	12
2.3 Synthetic Hydroxyapatite	13
2.3.1 <i>Crystallography of HAp</i>	13
2.3.2 <i>Synthesis by Precipitation (Brief)</i>	14
2.3.3 <i>Sol-Gel Synthesis</i>	15
2.3.4 <i>Synthesis by Solid State Reaction</i>	15
2.3.5 <i>Microemulsion Production Technique</i>	16
2.3.6 <i>Hydrothermal Conversion of Coral to Hydroxyapatite</i>	16
2.4 Synthetic Hydroxyapatite – Precipitation Method (Detailed)	17
2.4.1 <i>Synthesis Temperature</i>	17

2.4.2	<i>Influence of pH</i>	19
2.4.3	<i>Maturation Time</i>	19
2.4.4	<i>Calcining</i>	20
2.4.5	<i>Sintering</i>	21
2.4.6	<i>Thermoanalytical Investigation</i>	22
2.4.7	<i>Improving Mechanical Properties</i>	22
2.4.8	<i>Hydroxyapatite-Collagen Composite</i>	23
2.5	Carbon Nanotubes	24
2.5.1	<i>Single-Walled Carbon Nanotubes</i>	26
2.5.2	<i>Multi-Walled Carbon Nanotubes</i>	27
2.5.3	<i>Synthesis of Multi-walled Carbon Nanotubes</i>	30
2.5.4	<i>Synthesis of Single-Walled Carbon Nanotubes</i>	33
2.5.5	<i>Purification of Carbon Nanotubes</i>	34
2.5.6	<i>Advantages of Nanotubes</i>	35
2.6	Hydroxyapatite Composites	35
2.6.1	<i>Fibre Composites</i>	36
2.6.2	<i>Hydroxyapatite – Carbon Nanotube Composite</i>	36
2.6.3	<i>Nanotube and Matrix Bonding</i>	37
2.6.4	<i>Fibre Aspect Ratio</i>	38
2.6.5	<i>Studies Reported Since 2004</i>	39
3.0	EXPERIMENTAL PROCEDURE	42
3.1	Materials	42
3.2	Overview of Procedures	42
3.3	Instrumentation and Techniques	43
3.3.1	<i>X-ray Diffraction</i>	44
3.3.2	<i>Neutron Diffraction</i>	44
3.3.3	<i>Small Angle Neutron Scattering</i>	48
3.3.4	<i>Synchrotron Diffraction</i>	49
3.3.5	<i>Rietveld Analysis</i>	53
3.3.5.1	<i>Whole Pattern Refinement – Rietveld Analysis</i>	53
3.3.5.2	<i>Rietveld Analysis of Synchrotron Data</i>	56
3.3.5.3	<i>Discrete Peak Analysis of Synchrotron Data</i>	59
3.3.6	<i>Transmission Electron Microscopy</i>	61
3.3.7	<i>Scanning Electron Microscopy</i>	62

3.3.8	<i>Bulk Density</i>	64
3.3.9	<i>Microhardness and Fracture Toughness</i>	64
3.3.10	<i>Nanoindentation</i>	66
3.3.11	<i>Surface Area</i>	67
3.3.12	<i>Thermal Analysis</i>	68
4.0	PRECIPITATION OF SYNTHETIC HYDROXYAPATITE	69
4.1	Precipitation Trials	69
4.1.1	<i>Calcium Hydroxide and Phosphoric Acid</i>	69
4.1.2	<i>Calcium Nitrate and Phosphoric Acid</i>	70
4.1.3	<i>Calcium Chloride and Phosphoric Acid</i>	71
4.1.4	<i>Calcium Chloride and Sodium Phosphate</i>	71
4.2	Chemical Precipitation	72
4.2.1	<i>Reagent concentration</i>	73
4.2.2	<i>Addition Rate and pH</i>	73
4.2.3	<i>Temperature and Maturation Time</i>	74
4.3	Further Processing	74
4.3.1	<i>Heat Treatment</i>	74
4.3.2	<i>Dense Sintered Pellet</i>	77
4.3.3	<i>Comparison with Commercial Powder</i>	81
4.3.4	<i>Sintered Pellet Diffraction Results</i>	84
4.4	Hot Isostatic Pressing	85
4.4.1	<i>HIP Pellet Diffraction Results</i>	88
5.0	FORMATION OF THE COMPOSITE	90
5.1	Purification of CNT Material	90
5.1.1	<i>Liquid purification</i>	90
5.1.2	<i>Gas phase purification</i>	93
5.2	Precipitation of Composite Material	95
5.2.1	<i>Refinement Results for precipitated HAp + 5% C post HIP</i>	98
5.3	Mechanically Mixed Composite Material	104
5.3.1	<i>Synthesised Composite</i>	104
5.3.2	<i>Commercial Material</i>	105
6.0	MECHANICAL PROPERTIES	113
6.1	Material Characterisation	113
6.2	Young's Modulus	121

6.2.1	<i>Comparison of Hardness</i>	126
6.3	Grain Size	129
6.3.1	<i>Surface Area</i>	132
6.4	Small Angle Neutron Scattering	133
7.0	SYNCHROTRON DIFFRACTION DATA ANALYSIS	136
7.1	Wavelength Determination	137
7.2	Whole Pattern Refinement – Rietveld Analysis Results	140
7.2.1	<i>Crystallite Size and Strain</i>	142
7.3	Discrete Peak Analysis Results	144
7.3.2	<i>Crystallite Size and Strain</i>	146
7.3.3	<i>Polished HAp sample</i>	149
7.4	Phase Purity	150
7.5	Lattice Parameters	157
8.0	SUMMARY AND CONCLUSIONS	159
	APPENDIX A	164
	APPENDIX B	165
	APPENDIX C	169
	REFERENCES	171

LIST OF FIGURES

Figure 1.1	Proposed research plan.	3
Figure 2.1	Partially sectioned humerus (arm bone).	5
Figure 2.2	The spongy bone tissue of the epiphysis and metaphysis contains red bone marrow, whereas the medullary cavity of the diaphysis contains yellow bone marrow.	7
Figure 2.3	Phase diagram of CaO-P ₂ O ₅ -H ₂ O system.	14
Figure 2.4	Drawing of a) a zig-zag nanotube that can be generated by dividing one half of a C ₆₀ molecule parallel to the three-fold axes and b) an armchair nanotube that can be generated by dividing one half of a C ₆₀ molecule parallel to the five-fold axes.	25
Figure 2.5	Drawing of carbon nanotubes with a) zig-zag, b) armchair, and c) helical/chiral structures.	26
Figure 2.6	Typical sample of single-walled nanotubes with a) general area, showing tubes coated with amorphous carbon, and b) higher magnification image of individual tubes.	27
Figure 2.7	TEM image of a) general area, showing multi-wall nanotubes tubes containing soot. Scale bar 100 nm. b) higher magnification image of individual tubes. Scale bar 10 nm.	28
Figure 2.8	High resolution TEM micrograph of a multi-walled nanotube with an ‘internal cap’. Scale bar 5 nm.	29
Figure 2.9	TEM image of a multi-walled nanotube cap closing the tube. Scale bar 5 nm.	29
Figure 3.1	A comparison of a) X-ray and b) neutron scattering amplitudes.	45
Figure 3.2	HRPD and MRPD resolution curves. Resolution curves for typical laboratory X-Ray Diffractometers and Synchrotron X-ray Diffractometers are included for comparison.	46
Figure 3.3	High Resolution Powder Diffractometer installed at ANSTO.	47
Figure 3.4	Ancillary: P1100 furnace at ANSTO, samples are loaded from above.	47

Figure 3.5	Top and side view of the major optical components on the 1-BM beamline, indicating their distance (metres) from the source, and the location of the experiment stations.	50
Figure 3.6	The absorption edge of a molybdenum foil.	51
Figure 3.7	Custom-designed sample holder and spinner mounted in station C on 1-BM at the Advanced Photon Source, photographed a) from the side and b) from above.	52
Figure 3.8	An observed diffraction peak $h(x)$ is a convolution between ‘pure’ specimen $f(y)$ and instrumental $g(z)$ contributions.	57
Figure 3.9	Vickers hardness testing technique, a) diamond indenter and b) shape of perfect indent.	65
Figure 3.10	a) Berkovich diamond indenter and b) shape of indent.	66
Figure 4.1	Selected 2-theta range from an XRD plot of data collected from the oven-dried powder produced by calcium hydroxide and phosphoric acid. The upper row of blue peak markers correspond to the HAp phase, and the lower row are highlighting the brushite impurity.	70
Figure 4.2	Selected 2-theta range of the XRD data collected for the calcium chloride and phosphoric acid reaction, with the blue peak markers showing the HAp phase (upper), as well as the brushite (middle) and monetite (lower) impurities.	71
Figure 4.3	In-situ neutron diffraction (MRPD) data deliberately offset on vertical scale over a selected 2-theta range: comparison of pure HAp powder after a) drying, b) heat treatment at 650 °C and c) heat treatment at 800 °C.	75
Figure 4.4	Lattice parameter a of HAp with increasing temperature, refined using models from the in-situ MRPD neutron diffraction data.	76
Figure 4.5	Lattice parameter c of HAp with increasing temperature, refined using models from the in-situ MRPD neutron diffraction data.	76
Figure 4.6	Transmission electron micrographs of a) HAp precipitate and b) heat-treated HAp powder.	78
Figure 4.7	X-ray diffraction data deliberately offset on vertical scale over a selected 2-theta range: comparison of c) pure HAp powder after drying, b) heat treatment at 650 °C and a) heat-treatment at 1100 °C.	79

Figure 4.8	HRPD neutron diffraction data (deliberately offset on vertical scale) showing a comparison of pure HAp powder material after b) drying at 110 °C for 24 hours, and a) after heat-treating at 650 °C for 4 hours.	80
Figure 4.9	SEM image of the sintered pure HAp pellet.	81
Figure 4.10	Neutron diffraction data deliberately offset on vertical scale - comparison between the a) pure HAp heat-treated powder and b) commercial HAp powder (Merck).	82
Figure 4.11	The Rietveld refinements for the neutron diffraction data collected from single phase sintered HAp pellets. The observed plot is black, the calculated plot is red, the difference plot is green and the blue lines represent the peak position markers for a hexagonal hydroxyapatite, $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$ phase.	85
Figure 4.12	Photograph of the a) laboratory synthesised HAp and the b) commercial HAp after the HIP process.	87
Figure 5.1	Transmission electron micrograph of a multi-wall nanotube found in the commercial CNT material, with associated profile of image intensity across the width of the nanotube.	91
Figure 5.2	Transmission electron micrographs of a) carbon material, and b) material after liquid purification. The scale bar is 0.2 μm for both images to allow for CNT length comparison to show the effect of the amount of oxidation in the liquid purification process.	92
Figure 5.3	TGA-DTA of the carbon CNT material in an a) air atmosphere and b) argon atmosphere.	94
Figure 5.4	Transmission electron micrograph of CNT material after gas phase purification in an argon environment. The scale bar shown is 20 nm to demonstrate that the CNTs are closed, hence undamaged during the purification process.	95
Figure 5.5	a) SEM and b) TEM micrographs of the precipitated HAp+CNT composite powder material after heat-treatment.	96
Figure 5.6	XRD data collected from the CNT material on a low-background sample holder.	97
Figure 5.7	MRPD neutron diffraction data collected during the heat-treatment of a powder HAp + 5% C composite material, where CNT material was	

	added to the $\text{Ca}(\text{NO}_3)_2$ reactant before precipitation occurs. The loss of graphite is apparent at 28.1° 2-theta.	98
Figure 5.8	HRPD neutron diffraction data over a selected 2-theta range collected from a powder HAp + 5% C composite material c) before heating, after heating to a) 900°C in air, and b) 900°C in a vacuum. Only a small amount of graphite at 31.8° 2-theta is oxidised when sample is heated in an inert atmosphere.	99
Figure 5.9	The result of the Rietveld refinement of the model calculated from the neutron diffraction data of HAp + 5% C after the HIP process. The observed plot is black, the calculated plot is red, the difference plot is green and the blue lines represent the peak position markers for the hydroxyapatite phase. Light blue shaded areas correspond to the excluded regions.	100
Figure 5.10	SEM micrographs of the precipitate HAp+CNT composite post HIP a) low magnification backscattered image showing the distribution of CNTs, and b) secondary electron image at high resolution showing a clump of the CNTs.	102
Figure 5.11	An evaporative carbon coated HAp+CNT sample, post HIP, showing the thickening of the CNTs.	103
Figure 5.12	SEM micrograph of the mechanically mixed HAp+CNT composite powder material after heat-treatment.	104
Figure 5.13	The result of the Rietveld refinement of the model calculated from the neutron diffraction data of HAp + 5% C mechanically mixed composite post HIP. The observed plot is black, the calculated plot is red, the difference plot is green and the blue lines represent the peak position markers for the hydroxyapatite phase. Light blue shaded areas correspond to the excluded regions of the unidentified impurity phase.	105
Figure 5.14	SEM micrographs of the mechanically mixed composites post HIP with a) 5% C, b) 12% C and c) 25% C.	107
Figure 5.15	Zeiss Supra 55VP SEM image of an un-coated HAp + 12% C post HIP sample, showing CNT incorporation into the HAp.	108
Figure 5.16	JEOL 2010F FEG-TEM image of an un-coated HAp + 12% C post HIP sample, showing CNT incorporation into the HAp.	108

- Figure 5.17 HRPD data collected from mechanically mixed HIP composite samples with A) 0%, B) 5%, C) 12%, and D) 25% C by weight. 109
- Figure 5.18 The result of the Rietveld refinements for the neutron diffraction data from a) commercial HAp, b) HAp + 5% C, c) HAp + 12% C, and d) HAp + 25% C after the HIP process. The observed plot is black, the calculated plot is red, the difference plot is green and the blue lines represent the peak position markers for the hydroxyapatite phase. Light blue shaded areas correspond to the excluded regions. 110
- Figure 6.1 Scanning Electron Micrographs of the HAp+12%C composite material at a) low, and b) high magnification, looking at the intersection of the CNT material and the HAp phase. 117
- Figure 6.2 Optical micrographs immediately after indentation of a) the commercial pure HAp sample and b) laboratory synthesised pure HAp sample. 119
- Figure 6.3 (i) the sharp point produces inelastic, irreversible deformation; (ii) at a critical load, flaws within the deformation become unstable, and subsurface radial cracks form on tensile median planes (the load axis); (iii) on increased loading, the crack propagates downward; (iv) on unloading, the median crack closes up below the surface but opens in the tensile field as the contact recovers its elastic component; (v) just prior to removal of the indenter, the tensile field dominates further expanding the surface radial cracks, and initiating a second system of sideways spreading lateral cracks; (vi) the expansion continues until the indenter is removed. 120
- Figure 6.4 Optical micrograph immediately after indentation of the commercial HAp + 5% C (2% CNT) composite sample. 121
- Figure 6.5 Load versus displacement for loading and unloading with a Berkovich indenter, where: h_r = depth of the residual impression; h_t = depth from the original sample surface at load P_t ; h_e = elastic displacement during unloading; h_p = 'plastic depth' of penetration; h_a = distance from the edge of the contact to the sample surface at full load. 122
- Figure 6.6 A comparison of the penetration depth reached with an indenter load of 100 mN for all of the samples. 124
- Figure 6.7 Load versus displacement for the laboratory synthesised pure HAp (red) and the commercial pure HAp (blue). 125

Figure 6.8	Load versus displacement for the commercial HAp mechanically mixed composite materials with an increase in the C content.	126
Figure 6.9	Comparison between the hardness results from the Vickers indentation and the Nanoindentation methods.	127
Figure 6.10	The hardness versus load curve (indentation size effect) has a distinct transition to a plateau hardness for a) Vickers hardness determined through microindentation, and b) hardness determined through nanoindentation.	128
Figure 6.11	Scanning Electron Micrographs of the grains boundaries for the a) pure sintered material, and b) HIP commercial material.	130
Figure 6.12	A plot of the grain size against Vicker's Hardness for the HIP samples.	132
Figure 6.13	SANS data collected from several pure HAp samples, a HAp+5%C mixed sample and a HAp+5%C precipitated sample.	134
Figure 7.1	Collected SRD data from the LaB ₆ standard reference material.	138
Figure 7.2	Wavelength calibration plot for XOR-1BM using LaB ₆ NIST standard 660a.	139
Figure 7.3	A selected 2-theta region from the Rietveld refinements for the models of the SRD data collected from commercial HAp material post HIP. The observed plot is black, the calculated plot is red, and the blue lines underneath the plot represent the peak position markers for a hexagonal hydroxyapatite, [Ca ₁₀ (PO ₄) ₆ (OH) ₂] phase. The shaded aqua-blue regions highlight an example of the small peaks that are unaccounted for by the HAp phase.	144
Figure 7.4	Plot of the Discrete Peak Analysis (averaged) and Rietveld analysis results of the crystallite size (nm) and respective errors for each of the ten samples.	147
Figure 7.5	Plot of the Discrete Peak Analysis (averaged) and Rietveld analysis results of the strain (%).	148
Figure 7.6	A portion of the synchrotron diffraction data collected from a) the LaB ₆ sample representing the instrumental contribution to the peak widths, b) the synthesised HAp sample, and c) the commercial HAp polished sample.	150

- Figure 7.7 X-ray, neutron and synchrotron diffraction data collected from the synthesised HAp + 5% C physically mixed sample, deliberately offset on vertical scale. The $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ and the $\beta\text{-Ca}_3(\text{PO}_4)_2$ phases have been labelled. 152
- Figure 7.8 Unit cell of the a) pure hexagonal hydroxyapatite phase and b) rhombohedral whitlockite impurity phase. Phosphate atoms are green, calcium blue, oxygen red, and hydrogen white. 154
- Figure 7.9 The Rietveld refinement of the models over the a) full and b) selected 2-theta range for the SRD data collected from the synthesised HAp + 5% C mixed sample. The observed plot is black, the calculated plot is red, the difference plot is green, the upper set of blue lines underneath the plot represent the peak position markers for a hexagonal hydroxyapatite phase [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$], and the lower set are for the rhombohedral beta – calcium phosphate phase, [$\beta\text{-Ca}_3(\text{PO}_4)_2$]. The shaded aqua-blue region is the exclusion of the CNT material. 155
- Figure 7.10 Plot of the a and c lattice parameters from the models in the Rietveld analysis for the SRD data. 158
- Figure A1 The result of the Rietveld refinements for the neutron diffraction data from a) commercial HAp, b) HAp + 5% C, c) HAp + 12% C, and d) HAp + 25% C after the HIP process. The observed plot is black, the calculated plot is red, the difference plot is green and the blue lines represent the peak position markers for the hydroxyapatite phase. Light blue shaded areas correspond to the excluded regions. 170

LIST OF TABLES

Table 2.1	Calcium Phosphate Phases	10
Table 3.1	Parameters that can be simultaneously refined in the Rietveld Method.	54
Table 4.1	Lattice parameters a and c of the pure HAp powder, refined using models from the in-situ heat-treatment MRPD neutron diffraction data.	75
Table 4.2	Refinement results from Rietveld modelling with a Voigt line profile for the neutron diffraction data collected from the heat-treated synthetic HAp powder and the commercial HAp powder samples.	82
Table 4.3	Refined parameters from Rietveld modelling with a Voigt line profile for the neutron diffraction data collected from the laboratory synthesised HAp and the commercial HAp.	83
Table 4.4	Refinement results from Rietveld modelling with a Voigt line profile for the neutron diffraction data from the sintered powder samples.	85
Table 4.5	Size reduction (%) in the samples after the HIP process. The initial diameter of the samples was 35.55 mm.	86
Table 4.6	Structural parameters and refinement results from Rietveld modelling with a Voigt line profile for the neutron diffraction data collected from the HIP pellets.	88
Table 5.1	Refinement results from Rietveld modelling with a Voigt line profile for the neutron diffraction data from the post HIP samples.	99
Table 5.2	Structural parameters from Rietveld modelling with the neutron diffraction data from the post HIP samples (for this, and all tables in this chapter, the values in parentheses correspond to the uncertainty in the least significant figure to the left).	101
Table 5.3	Structural parameters and refinement results from Rietveld models of the neutron diffraction data from the post HIP samples with increased concentration of CNTs.	112
Table 6.1	HIP samples prepared for mechanical property testing.	114

Table 6.2	Density, percentage of theoretical density, Vickers hardness (VH) and indentation fracture toughness (KIC) of each of the seven samples (for this and all tables in this chapter, the values in parentheses correspond to the uncertainty in the least significant figure to the left).	116
Table 6.3	Penetration depth, Hardness and Young's Modulus measured for each of the seven samples using nanoindentation.	123
Table 6.4	Average grain size and the microhardness of the seven HIP samples and a sintered HAp sample measured from SEM micrographs, as well as a precipitate HAp sample measured from TEM micrographs.	131
Table 6.5	BET surface area measurements for the laboratory synthesised pure HAp and the laboratory synthesised HAp + 5%C composite HIP materials.	133
Table 6.6	Results from the linear functions fitted to the SANS data in Figure 6.13.	133
Table 7.1	Description of the samples analysed with SRD.	137
Table 7.2	Refined parameters from Rietveld modelling with a Voigt line profile for the synchrotron diffraction data (for this and all tables in this chapter, the values in parentheses correspond to the uncertainty in the least significant figure to the left).	141
Table 7.3	Crystallite size and strain calculated from the integral line breadths of four discrete sets of Miller Indices for the eleven samples.	145
Table 7.4	Critical factors that need to be controlled during the precipitation process to produce a pure HAp material.	151
Table 7.5	Lattice, structural and thermal parameters of the β -Ca ₃ (PO ₄) ₂ phase refined from a model of the SRD data collected from the synthesised HAp + 5% C mixed sample.	156
Table 7.6	Lattice parameters a and c refined from a model of the SRD data	157
Table 8.1	Critical factors that need to be controlled during the precipitation process to produce a pure HAp material.	159
Table A1	Components of typical long bone.	164
Table A2	Generally accepted mechanical, electrical, optical, thermal and magnetic properties of CNTs.	165