Boron Nitride Nanotube Reinforced Titanium Matrix Composite

by

Md Mahedi Hasan Bhuiyan
(B.Sc. and M.Sc.)

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Abstract

Titanium (Ti) matrix composites are attractive engineered materials for structural applications to replace current steel and aluminium products, especially in automotive industries that consume large amounts of structural materials. A number of reinforcing fillers have been tested to improve the room and high temperature mechanical properties of Ti composites. However, none of them met the requirements for practical applications. Therefore, further investigation of new kinds of reinforcements for titanium matrix composites is of great interest.

Boron nitride nanotubes (BNNTs) possessing high strength and high oxidation resistance are a potential candidate for reinforcing Ti composites. Nevertheless, small scale synthesis of BNNTs using conventional techniques limits their use as fillers which is yet to be developed. Therefore, a specially designed rotating furnace has been employed in this research for the production of large quantity and high density nanotubes using ball milling and annealing method and the synthesis conditions have been optimized.

The produced BNNTs are used to reinforce Ti, following the conventional pressing and sintering method. The effects of filler content and various sintering conditions on the microstructure and mechanical properties of the composites have been studied. The results are compared to Ti composites reinforced by hexagonal boron nitride (h-BN) particles. The formation of interfacial reaction products at Ti-BNNT interface and their subsequent growth behaviour was also studied. This was performed by preparation of Ti coated BNNT nanocomposites using the sputtering technique and then analysing the interface under different heat treatment conditions.

It was found that composites sintered at higher temperatures resulted in in-situ formed TiB phase in the microstructure at the expense of BNNTs due to the reaction between BNNTs and Ti. The reinforcing nanotubes, particles and in-situ formed second phase reduced the grain sizes in the microstructure and rendered improved mechanical properties of the composites. The investigation of nanocomposite interface revealed that TiB2 nanocrystal initially forms at Ti-BNNT interface and most of them are subsequently transformed to TiB phase with the extent of sintering periods. This suggests that hot consolidation of powders with short processing time would be more beneficial for producing BNNT reinforced Ti matrix composites.
# Table of Contents

Abstract ........................................................................................................................... i

Table of Contents ........................................................................................................... ii

List of Figures .............................................................................................................. v

List of Tables ............................................................................................................... xi

1 *Introduction* ............................................................................................................ 1

1.1 Thesis Structure .................................................................................................. 4

2 *Literature Review* ................................................................................................. 5

2.1 Introduction ........................................................................................................ 5

2.2 Titanium ............................................................................................................. 5

2.2.1 Physical Properties ....................................................................................... 5

2.2.2 Phases and Microstructures ......................................................................... 6

2.2.3 Applications .................................................................................................. 8

2.2.4 Manufacturing Techniques ......................................................................... 8

2.3 Powder Metallurgy System .............................................................................. 9

2.3.1 Effect of Raw Powders ............................................................................... 9

2.3.2 Mixing of Powders ...................................................................................... 10

2.3.3 Powder Consolidation ................................................................................ 11

2.4 Titanium Matrix Composites (TMC) ............................................................. 12

2.4.1 Selection of Reinforcement ....................................................................... 13

2.4.2 Interfacial Reactions .................................................................................... 14

2.4.3 Types of Reinforcements .......................................................................... 14

2.4.4 Particle Reinforced Composites ................................................................. 15

2.4.5 In-situ Formed Reinforcing Composites ................................................... 19

2.4.6 Nanotube Reinforced Composites .............................................................. 25

2.5 Boron Nitride Nanotube (BNNT) ................................................................... 31

2.5.1 Advantages of BNNT over CNT ................................................................. 32

2.5.2 Synthesis of BNNT .................................................................................... 33

2.5.3 BNNT Reinforced Metal Matrix Composites ........................................... 39

2.6 Summary .......................................................................................................... 43

3 *Experimental Techniques* .................................................................................... 45

3.1 Introduction ........................................................................................................ 45

3.2 Material Processing and Synthesis .................................................................... 45

3.2.1 Ball Milling .................................................................................................. 45

3.2.2 Glove Box ................................................................................................... 48

3.2.3 Sputtering Machine .................................................................................... 49
4 Synthesis of Large Quantity and High Density Boron Nitride Nanotubes......................................................................................... 65
  4.1 Introduction .................................................................................. 65
  4.2 Experimental ............................................................................... 66
  4.3 Results and Discussion ................................................................ 67
    4.3.1 Conventional Nanotube Synthesis ........................................ 67
    4.3.2 Nanotube Synthesis with Rotating Furnace .......................... 69
  4.4 Conclusion .................................................................................. 80

5 Boron Nitride Particle Reinforced Titanium Matrix Composite............................. 81
  5.1 Introduction .................................................................................. 81
  5.2 Experimental ............................................................................... 82
  5.3 Results and Discussion ................................................................ 83
    5.3.1 Powder Morphologies, Mixing and Phases ............................ 83
    5.3.2 Composite Microstructures and Phases ............................... 86
    5.3.3 Mechanical Properties of Composites ................................ 92
    5.3.4 Evaluation of Composite Fracture Surfaces ......................... 97
  5.4 Conclusion .................................................................................. 101

6 Boron Nitride Nanotube Reinforced Titanium Matrix Composite 103
  6.1 Introduction .................................................................................. 103
  6.2 Experimental ............................................................................... 103
  6.3 Results and Discussion ................................................................ 104
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.3.1</td>
<td>Boron Nitride Nanotubes</td>
<td>104</td>
</tr>
<tr>
<td>6.3.2</td>
<td>Purification of the Nanotubes</td>
<td>106</td>
</tr>
<tr>
<td>6.3.3</td>
<td>Composite Powder Mixtures</td>
<td>109</td>
</tr>
<tr>
<td>6.3.4</td>
<td>Microstructure and Phases of Composites</td>
<td>111</td>
</tr>
<tr>
<td>6.3.5</td>
<td>Room Temperature Mechanical Properties</td>
<td>117</td>
</tr>
<tr>
<td>6.3.6</td>
<td>High Temperature Mechanical Properties</td>
<td>121</td>
</tr>
<tr>
<td>6.3.7</td>
<td>Fracture Surface of Composites</td>
<td>125</td>
</tr>
<tr>
<td>6.3.8</td>
<td>Transmission Electron Microscopy of the Composites</td>
<td>129</td>
</tr>
<tr>
<td>6.3.9</td>
<td>Effects of h-BN and BNNT Reinforcements</td>
<td>139</td>
</tr>
<tr>
<td>6.4</td>
<td>Conclusion</td>
<td>140</td>
</tr>
</tbody>
</table>

**7 Interfacial Reaction between Titanium and Boron Nitride Nanotubes**

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1</td>
<td>Introduction</td>
<td>142</td>
</tr>
<tr>
<td>7.2</td>
<td>Experimental</td>
<td>143</td>
</tr>
<tr>
<td>7.3</td>
<td>Results and Discussion</td>
<td>144</td>
</tr>
<tr>
<td>7.3.1</td>
<td>Nucleation, Growth and Morphology of Reaction Products</td>
<td>144</td>
</tr>
<tr>
<td>7.3.2</td>
<td>Effect of Reaction Products on the Mechanical Properties</td>
<td>155</td>
</tr>
<tr>
<td>7.4</td>
<td>Conclusion</td>
<td>155</td>
</tr>
</tbody>
</table>

**8 Conclusion**

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.1</td>
<td>Suggestions for Future Works</td>
<td>159</td>
</tr>
</tbody>
</table>
List of Figures

Figure 2.1: Schematic representation of alloying elements on phases of titanium [43] ... 7
Figure 2.2: Binary phase diagram for (a) Ti-B and (b) Ti-N systems [55] ...................... 16
Figure 2.3: Reactions and phase formations between Ti and BN [84] ........................... 17
Figure 2.4: Morphology of TiB whiskers; ...................................................................... 20
Figure 2.5: Schematic diagram of (a) B27 crystal structures for TiB ............................. 21
Figure 2.6: Construction of TiB and TiB2 crystal structure ............................................ 22
Figure 2.7: The appearance of TiB whiskers with respect to volume fraction [101, 102] ......................................................................................................................................... 23
Figure 2.8: Schematic of “catalytic capillarity mechanism” ........................................... 36
Figure 2.9: Schematic of “root growth mechanism” for nanotube growing [194] ......... 37
Figure 3.1: Schematic of the vertical high-energy ball milling machine ...................... 46
Figure 3.2: Schematic diagram of planetary ball milling machine ................................. 47
Figure 3.3: Fritsch P-7 milling machine, milling jar and balls used to mix the powders 47
Figure 3.4: Nitrogen gas filled glove box for handling ball milled powders ................. 49
Figure 3.5: Die and punch arrangement for pressing powder ........................................ 50
Figure 3.6: Shop press machine to consolidate powders ................................................ 51
Figure 3.7: Schematic of cylindrical compact after pressing the powders ..................... 51
Figure 3.8: Schematic diagram of rotating furnace ......................................................... 52
Figure 3.9: Specially designed rotating furnace .............................................................. 53
Figure 3.10: Differences in the controller temperature ................................................... 53
Figure 3.11: (a) Sintered composites (b) machined composites ..................................... 55
Figure 3.12: Creation of interaction volume and appearance of various energy .......... 60
Figure 3.13: Set-up for density measurement by Archimedes method ......................... 62
Figure 3.14: Arrangement of room temperature compression test ................................. 63
Figure 3.15: Arrangement of high temperature compression test ................................. 64
Figure 4.1: BNNTs synthesized with the horizontal tube furnace; (a) low magnification and (b) high magnification.................................................................................................................67

Figure 4.2: XRD pattern of BNNTs synthesized with the horizontal tube furnace .......68

Figure 4.3: Sintered BN particles underneath the synthesized nanotubes ..................69

Figure 4.4: Boron nitride nanotubes from rotating furnace annealed at 1100°C for 3 h; (a) low magnification and (b) high magnification..........................................................................................69

Figure 4.5: XRD pattern of BNNTs synthesized with rotating furnace at 1100°C for 3 h .........................................................................................................................................70

Figure 4.6: Formation of agglomerations in the form of large spherical particles; .......71

Figure 4.7: XRD patterns obtained from nanotubes synthesized at (a) 1100°C for 6 h .72

Figure 4.8: SEM images of nanotube synthesized under various annealing temperatures and time; (a, b) 1100 °C, 6 h (c, d) 1200°C, 3h (e, f) 1200 °C, 5h (g, h) 1300 °C, 1 h ..73

Figure 4.9: XRD pattern of the nanotubes synthesized under optimized annealing condition of 1200 °C for 3 h; B powders are inserted at (a) room temperature (b) 1200°C and (c) room temperature with steel balls.........................................................................................74

Figure 4.10: Morphology and yield of nanotubes synthesized at 1200 °C for 3 h by introducing ball milled powers at (a, b) 1200°C (c, d) room temperature with steel balls and (e, f) 1200°C with steel balls..................................................................................................................75

Figure 4.11: XRD traces of the nanotubes obtained at 1200°C for 1 h with gas flow rate .................................................................................................................................................76

Figure 4.12: Low magnification and high magnification images of nanotubes obtained at 1200°C for 1 h with gas flow rate (a, b) 2 l/min and (c, d) 4 l/min.................................77

Figure 5.1: Starting (a, b) Ti powders and (c, d) h-BN powders; ................................83

Figure 5.2: XRD pattern obtained from (a) Ti powders and (b) h-BN powders.............84

Figure 5.3: Distribution of h-BN powder in Ti-5vol%BN powder composition ............85

Figure 5.4: Relative density of h-BN reinforced Ti composites .....................................86

Figure 5.5: XRD pattern obtained from composites sintered at (a) 800°C for 1 h (b) 1000°C for 1 h (c) 1000°C for 3 h and (d) enlarged view of Ti-5vol%BN composition for comparison; (i) pure Ti (ii) Ti-0.5vol%BN (iii) Ti-1vol%BN (iv) Ti-2vol%BN (v) Ti-3vol%BN (vi) Ti-4vol%BN (vii) Ti-5vol%BN .................................................................87
Figure 5.6: Cross-sectional microstructure of the composite sintered at 800°C for 1 h (a) pure Ti (b) Ti-1vol%BN (c) Ti-3vol%BN (d) Ti-5vol%BN ........................................... 89

Figure 5.7: Cross-sectional microstructure of the composite sintered at 1000°C for 1 h (a) pure Ti (b) Ti-1vol%BN (c) Ti-3vol%BN (d) Ti-5vol%BN .................................................. 89

Figure 5.8: Cross-sectional microstructure of the composite sintered at 1000°C for 3 h (a) pure Ti (b) Ti-1vol%BN (c) Ti-3vol%BN (d) Ti-5vol%BN .................................................. 90

Figure 5.9: Average grain size of composites as a function of ....................................... 90

Figure 5.10: Distribution of TiB phase in (a) Ti-0.5vol%BN and (b) Ti-5vol%BN composites sintered at 1000°C for 3 h; (c) thin long TiB needles with high aspect ratio (d) Short and thick TiB plates (e) slab like TiB plates (f) cluster of TiB needles .......... 91

Figure 5.11: Comparison of hardness obtained from the composites.............................. 93

Figure 5.12: Representative stress-strain curve obtained from room temperature compression test of the composites sintered at (a) 800°C for 1 h (b) 1000°C for 1 h .... 95

Figure 5.13: (a) Maximum compressive strength and (b) reduction of length of the composites with respect to sintering conditions and reinforcement content......................... 96

Figure 5.14: Fracture surfaces of Ti-5vol%BN composite sintered at 800°C for 1 h; (a) low magnification image of fracture surface (b) high magnification image showing ductile type fracture (c) distribution of h-BN particles in the matrix (d) structural integrity of h-BN particles (e) cluster of h-BN particles (f) reaction at Ti-BN interface 97

Figure 5.15: Fracture surfaces from Ti-3vol%BN composite sintered at 1000°C for 1 h; (a) low magnification and (b) high magnification image of fracture surface (c) retained h-BN particles (d) BN particles pull out from matrix (e) randomly oriented TiB whiskers (f) pull out of TiB whiskers from the matrix during deformation ....................... 98

Figure 5.16: Fracture surfaces from Ti-3vol%BN composite sintered at 1000°C for 3 h; (a) low and (b) high magnification image (c) occurrence of ductile fracture in the region where h-BN particles and TiB whiskers are absent (d) in-situ formed TiB whiskers .... 99

Figure 6.1: SEM image of as synthesized boron nitride nanotubes; ......................... 105

Figure 6.2: TEM image of (a) bamboo structured and (b) cylindrical structured........ 105

Figure 6.3: XRD pattern from synthesized boron nitride nanotubes ......................... 106

Figure 6.4: The synthesized nanotubes entangled in the form of large particles; .......... 107
Figure 6.5: Agglomerated particles remained after mixing with Ti powders; ........... 107

Figure 6.6: Boron nitride nanotubes extracted after ultrasonication at (a) 30 min ....... 108

Figure 6.7: Residual particles after 120 min ultrasonication; .................................... 108

Figure 6.8: Distribution of BNNTs in Ti powders after mixing; (a, b) individual BNNTs on Ti particle surface (c) cluster of BNNTs filling void spaces within Ti powders and (d) low magnification image of showing homogeneous distribution of BNNTs .......................................................................................................................... 109

Figure 6.9: XRD pattern obtained from the mixture of Ti and BNNTs; (a) Pure Ti (b) Ti-0.5vol%BNNT (c) Ti-1vol% BNNT (d) Ti-2vol%BNNT (e) Ti-3vol%BNNT (f) Ti-4vol%BNNT and (g) Ti-5vol%BNNT .......................................................................................................................... 110

Figure 6.10: Relative density of titanium matrix composites with BNNT content .... 111

Figure 6.11: XRD pattern obtained from the composite sintered at (a) 800°C for 1 h (b) 1100°C for 3 h (c) 1200°C for 3 h and (d) 1200°C for 3 h; (i) pure Ti (ii) Ti-0.5vol%BNNT (iii) Ti-1vol%BNNT (iv) Ti-2vol%BNNT (v) Ti-3vol%BNNT ......... 112

Figure 6.12: XRD trace for Ti-5vol%BNNT composite sintered at (a) 800°C for 1 h (b) 1000°C for 3h (c) 1100°C for 3 h and (d) 1200°C for 3 h ............................................ 113

Figure 6.13: Cross-sectional microstructure of composite sintered at 800°C for 1 h; (a) pure Ti (b) Ti-1vol%BNNT (c) Ti-3vol%BNNT .......................................................... 114

Figure 6.14: Cross-sectional microstructure of composite sintered at 1000°C for 3 h; (a) pure Ti (b) Ti-1vol%BNNT (c) Ti-3vol%BNNT .......................................................... 114

Figure 6.15: Cross-sectional microstructure of composite sintered at 1100°C for 3 h; (a) pure Ti (b) Ti-1vol%BNNT (c) Ti-3vol%BNNT .......................................................... 115

Figure 6.16: Cross-sectional microstructure of composite sintered at 1200°C for 3 h; (a) pure Ti (b) Ti-1vol%BNNT (c) Ti-3vol%BNNT .......................................................... 115

Figure 6.17: Average grain size with BNNT reinforcement and sintering conditions . 116

Figure 6.18: Morphology of in-situ formed TiB phase in Ti-5BNNT ...................... 117

Figure 6.19: Stress-strain curve from the room temperature compression test of composites sintered at (a) 800°C for 1 h (b) 1000° for 3 h (c) 1100° for 3 h and ....... 118

Figure 6.20: Room temperature (a) compressive strength and (b) reduction of length 119
Figure 6.21: Stress-strain curve obtained from compression test at 500°C for composites sintered at (a) 800°C for 1 h (b) 1000°C for 3 h (c) 1100°C for 3 h and (d) 1200°C for 3 h. 122

Figure 6.22: High temperature (a) compressive strength and (b) reduction of length at fracture. 122

Figure 6.23: Fracture surface of Ti-5vol%BNNT composite sintered at 800°C for 1 h; (a) ductile type fracture (b) low magnification image showing segregation of BNNTs (c) a cluster of BNNTs (d) BNNTs reacted in a few places (e) protruded BNNTs from the matrix after fracturing of composite (f) fragments of BNNTs in the matrix. 125

Figure 6.24: Fracture surface of Ti-5vol%BNNT composite sintered at 1000°C for 3 h; (a) partially reacted BNNTs with Ti (b) retained BNNTs after reaction (c) a long TiB whisker (d) pull out of TiB whiskers from the matrix (e) cleavage type fracture (f) ductile type fracture. 127

Figure 6.25: Fracture surface analysis of Ti-5vol%BNNT composite sintered. 128

Figure 6.26: EDX elemental mapping at Ti-BNNT interface in composites sintered at 800°C for 1 h; (a) bright field image and mapping of (b) Ti (c) B (d) N (e) O (f) C elements. 130

Figure 6.27: (a) Cluster of BNNTs (b) high resolution image of nanotube at point “P” and EDX elemental mapping of (c) Ti (d) B (e) N (f) Fe. 131

Figure 6.28: (a) Cross-section of TiB (b) EDX area analysis in that cross-section. 132

Figure 6.29: (a) TiB needle in the composite sintered at 800°C for 1 h (b) high resolution image from this needle (c) diffraction pattern from Ti matrix. 133

Figure 6.30: (a) TiB phases in composites sintered at 1000°C for 3 h (b) partially reacted BNNTs (c) EDX line profile in partially reacted nanotube. 134

Figure 6.31: (a) Bright field image of reacted nanotubes and EDX elemental. 135

Figure 6.32: (a) Randomly oriented TiB in the composite sintered at 1100°C for 3 h. 135

Figure 6.33: (a) Bright field image from the cross-section of a coarse TiB whisker. 136

Figure 6.34: Interactions with dislocations for strengthening the composites obtained from deformed samples; (a) presence of dislocations in the matrix; TiB-dislocation interactions in the composites sintered at (b) 1000°C for 3 h and (c) 1100°C for 3 h. 138
Figure 6.35: Comparison of maximum strength and corresponding ductility for h-BN and BNNT reinforced composites; (a) Compressive Strength (b) Reduction of Length
....................................................................................................................................... 139

Figure 7.1: SEM images of (a, b) Ti coated BNNTs and heat treated at ...................... 145

Figure 7.2: SEM images of Ti coated BNNTs heat treated at 800°C for 1 h; (a) low magnification image of agglomerates (b) reaction particles formed on the surfaces ... 146

Figure 7.3: SEM images of Ti coated BNNTs heat treated at 900°C for 1 h; (a) low magnification image of nanotube clusters (b & c) consumption of nanotube by reaction caused sectioning of nanotube at different locations (d) elongated and hexagonal prism like particles formed as a result of reaction .................................................................. 147

Figure 7.4: XRD patterns obtained from the heat treated nanocomposites ............... 147

Figure 7.5: SEM images of Ti coated BNNT nanocomposite heat treated............... 148

Figure 7.6: TEM images from the composites heat treated at 800°C for 30 min; ...... 149

Figure 7.7: TEM images of nanocomposites heat treated at 800°C for 1 h; (a) distribution of TiB$_2$ crystals on the BNNT surface (b) high resolution image from the BNNT side (c) high resolution of a TiB$_2$ crystal (d) lattice spacing and interfacial mismatch between BNNT and TiB$_2$ crystals ................................................................. 151

Figure 7.8: Dark field TEM images from the nanocomposites heat treated.......... 152

Figure 7.9: Schematic diagram of (a) TiB$_2$ crystal morphology......................... 153

Figure 7.10: SEM images of the nanocomposites after heat treatment .............. 154
List of Tables

Table 2.1: Physical properties of some pure metals used as structural materials [44]...... 6
Table 2.2: Properties of some reinforcing compounds currently in use [8, 64]............. 14
Table 2.3: Mechanical properties of c-BN/h-BN reinforced composites ....................... 18
Table 2.4: Comparison of mechanical properties of TiB reinforced Ti composites........ 23
Table 2.5: Mechanical properties of CNT reinforced titanium matrix composites ....... 30
Table 2.6: Property comparison between CNT and BNNT ............................................ 32
Table 2.7: Ball milling and annealing conditions for various BNNT synthesis ............ 38
Table 2.8: Mechanical properties of BNNT reinforced metal matrix composites ....... 42
Table 3.1: Ball milling conditions in vertical high-energy ball milling ....................... 46
Table 3.2: Optimized milling conditions for homogeneously mixing of powders ....... 48
Table 3.3: The conditions for sputtering operation ......................................................... 50
Table 3.4: Polishing conditions for composite samples .................................................. 57
Table 3.5: XRD performing conditions for various kinds of samples ....................... 58
Table 3.6: SEM imaging conditions for various kind of samples ............................... 60
Table 4.1: Effect of processing conditions on the synthesized boron nitride nanotubes 78
Table 4.2: Comparison of nanotube yield through various methods ............................. 79
Table 6.1: A comparison in the room temperature mechanical properties of TMC ..... 121
Table 6.2: A comparison in the high temperature mechanical properties of TMC....... 124
CHAPTER ONE

1 Introduction

In order to increase the fuel efficiency and therefore reduce energy consumption and greenhouse gas emission, the automotive and aerospace component parts need to be light but of essentially high strength as well as reliability.

Titanium (Ti) is an attractive material because of its high strength to weight ratio compared to aluminium and steel. It also possesses high corrosion resistance and good chemical inertness, which are desirable for structural materials [1, 2]. However, commercially pure Ti exhibits low wear resistance and poor high temperature strength [3, 4]. To minimize these drawbacks, a number of Ti alloys have been developed over the decades for manufacturing specific components that account for niche applications in aerospace industries [5, 6]. The applications of Ti products are mainly limited by the high cost of the material and its manufacturing [7]. The material cost can be lowered by adding alloying elements, which can be further minimized by using TiH₂ powders instead of commercially pure (CP) Ti powders. On the other hand, optimizing different processing conditions to obtain desired mechanical properties would boost the benefit-cost ratio and open a vast area of applications to automotive industries, gas turbine engine parts [6, 8, 9], military armoured vehicles [10], marine components, chemical industries and offshore drilling equipment [5, 6]. The biocompatibility of Ti also makes it suitable for biomedical application in orthopaedic implants [11, 12].

Although the incorporation of alloying element to Ti can impart specific properties such as strength, wear, fatigue and creep resistance, it also accounts for cost and weight. Therefore, there is a challenge to design new kinds of advanced materials, such as Ti matrix composites (TMC) that can perform in similar fashion. The development of Ti composites is of great recent interest for the international research community, especially for structural applications in automotive and aerospace component parts [13] that can be efficiently and reliably operated even at high temperatures [14]. The recent adoption of TiB reinforced Ti matrix composite (TMC) by Toyota Motors for the intake and exhaust valve [8] has spurred this investigation further. TMC, with the reduced weight and improved performance with high benefit-cost ratios, are gradually replacing Ti alloy materials for fabrication of components.
The microstructure and hence properties of the Ti composite are largely influenced by the type of fillers used in the composite. For discontinuously reinforced composites, the use of particles, whiskers, wires and nanotubes are commonplace. Fabrication of Ti matrix composites requires suitable reinforcement and should be selected depending on various criteria. Common reinforcements include SiC, Y2O3, Al2O3, Si3N4, B4C, TiB2 and CNT to enhance mechanical properties by dispersion hardening mechanism [8, 15]. However, employing these reinforcements in TMC could not meet all the requirements for practical applications in industries. The search for new kinds of reinforcement materials that could render enhanced mechanical properties, thus increasing benefit-cost ratio for industrial applications, is still underway.

One dimensional materials like nanotubes, nanowires and nanorods are now considered emerging reinforcements for composites due to their extraordinary physical and mechanical properties. Boron nitride nanotube (BNNT), a hard ceramic material which is structurally analogous to carbon nanotube (CNT) with B and N atoms arranged in hexagonal manner and wrapped into a tubular structure, can be potential fillers in Ti matrix composites. BNNTs possess a high elastic modulus of 750–1200 GPa [16, 17], a tensile strength greater than 24 GPa [18], oxidation resistance up to 700–900°C [19] and are able to withstand a good amount of deformations [20, 21]. Such attractive physical and mechanical characteristics of BNNTs recently triggered much research on BNNT reinforced polymer [22-28] and glass [29, 30] matrix composites. Despite having all these special features, reinforcement in metal matrix composite is still in its early stage. Only a few investigations have been conducted recently for aluminium matrix composites [31-35], while no research has been conducted on Ti to date. Incorporation of BNNTs in aluminium matrix greatly improved the mechanical properties. The interfacial reaction zone is also thinner and much more stable than other kinds of matrix-reinforcement interface. The high oxidation resistance of BNNTs would be an added advantage for high temperature applications of Ti matrix composites, for example as engine parts for vehicles. Therefore, BNNTs could be a suitable candidate for reinforcing Ti composites and their properties will be of great interest.

One obstacle of employing BNNTs as reinforcement in TMC is its reduced production capacity. Currently, BNNTs are synthesized on a small scale for laboratory experimental purposes. However, the preparation of composites requires a large quantity of high quality BNNTs. For industrial scale production of BNNT reinforced composites this requirement is even higher. Therefore, in order to realize the potentiality of BNNTs as fillers in
composites, it is necessary to devise a special manufacturing technique and equipment that can be used for the production of a large quantity and high density BNNTs.

For discontinuously reinforced composites, the control of microstructural homogeneity and reaction at the matrix-reinforcement interface is the most challenging issues in the preparation of Ti matrix composites. A thin reaction layer at the interface could be beneficial, but too much interfacial reaction can result in instability and brittleness during the load transfer from matrix to the reinforcements. A detailed study at the Ti-BNNT interface is also important to identify the earliest reaction product that might have evolved during thermo-mechanical treatment and growth with respect to various thermal treatment conditions.

Hexagonal boron nitrides (h-BN) in its particle form has a similar crystal structure to graphite and might also be a good candidate for reinforcement in Ti composites. Previously, these particles have mostly been reinforced in Ti for preparation of ceramic matrix composites to obtain superior mechanical properties [36, 37], such as TiN and TiB2 phases [38-42]. Employing h-BN particles as the reinforcement in this research would also help to distinguish the effects between nanotube and particle reinforcement on the microstructure and properties of the composites.

In this research, the composites were synthesized through the powder metallurgy route, as it gives the best opportunity to uniformly distribute the reinforcements within the matrix. The powder metallurgy process is able to produce a segregation free microstructure where density and melting temperature difference between the matrix and reinforcement is a major obstacle in the casting process. The powder metallurgy system also provides an opportunity to tailor the microstructure by controlling the grain growth and boundaries. In addition, near net shape manufacturing by powder metallurgy significantly reduces the wastage of materials during the machining process. Since the mechanical properties of Ti matrix composites are strongly dependent on the microstructure, which is influenced by the raw materials, compositions and processing conditions, it is necessary to establish a relationship between these parameters to optimize the performance of the composite.

The main objective of this thesis includes (i) synthesis of high quality boron nitride nanotubes at large scales for mass production of the Ti composites; (ii) manufacturing of boron nitride particle (h-BN) and nanotube (BNNT) reinforced Ti matrix composites; (iii) evaluation of mechanical properties of the composites at room and high temperatures with
respect to the reinforcement content and processing conditions; (iv) analysing the effects of particles, nanotubes and reaction phases on the microstructure and mechanical properties of the composites; (v) investigating the reaction mechanism and formation of phases between Ti and BNNTs.

1.1 Thesis Structure

Following on from this Introduction chapter, the second chapter reviews from the literature. This includes information about Ti and BNNTs, as well as the effects of various reinforcements, compositions and processing conditions on the mechanical properties of Ti alloys and composites. It also showed interfacial compounds and second phases formed in the microstructures and matrix-reinforcement interfaces.

The third chapter comprises various techniques and instruments employed to perform material synthesis, characterizations and property evaluation of the composites.

The fourth chapter demonstrates how to synthesize large quantity and high density BNNTs. The nanotubes were synthesized by ball milling and annealing method using a specially designed rotating furnace. Various annealing conditions were tested to optimize the yield of BNNTs.

Hexagonal boron nitride (h-BN) particle reinforced Ti matrix composites were introduced in the fifth chapter. They were prepared under different percentages and processing conditions. h-BN particles were reinforced to understand the different behaviour between particle and nanotube reinforced composites. The effects of particle reinforcement and second phases on the microstructure and mechanical properties of the composites were investigated.

The synthesised nanotubes were employed in chapter six to produce BNNT reinforced composites under different contents and processing conditions. The effects of nanotube reinforcement on the microstructure and mechanical properties were investigated. The formation and distribution of reaction phases were identified using fractography and transmission electron microscopy.

The interface between Ti and BNNTs was analysed in Chapter 7. The onset conditions for formation of the nucleated phase of phases and their growth behaviour as a function of thermal treatment were identified. An overall conclusion drawn from the research chapters and direction of future works are shown in Chapter 8.
2 Literature Review

2.1 Introduction
The unique physical characteristics of titanium alloys and composites have long been of research interest. Considering the volume of other kinds of structural materials such as steel and aluminium, titanium is still in niche applications. The gradual development of titanium alloy composites has already replaced many steel oriented component parts and widen its applications. Manufacturing of titanium composite is deemed to give multi-fold benefits in terms of weight reduction, processing cost and controlled mechanical properties compared to titanium alloys.

The aim of this chapter is to review the latest developments of different types of titanium composites. The microstructure and mechanical properties of these composites vary, depending on the type and morphology of the reinforcement, processing routes and conditions. The formation of second phase and interfacial reactions in limiting the mechanical properties is also discussed.

2.2 Titanium
2.2.1 Physical Properties
Titanium is an attractive structural material, due to its high specific strength, corrosion resistance and chemical inertness compared to its counterpart ferrous and aluminium alloys. However, its stiffness, fatigue and creep properties are still inferior to other structural materials. The wear and heat resistance properties of titanium are also poor compared with many other structural materials that are based on steel or nickel based alloys. The strength of pure titanium is low representing an elastic modulus of 110 GPa and an ultimate tensile strength of 550 MPa, which has prompted researchers to develop new kind of alloys and composites for practical applications. Titanium has a high affinity for oxygen that forms a rutile TiO$_2$ layer, which protects the material from further oxidation, corrosion and chemical reaction. This protective layer is unstable at a temperature above 550°C as high temperature decreases the solubility limit of oxygen due to slower diffusion process. The addition of Al increases the oxidation resistance as
it forms a thermally stable $\alpha$-$\text{Al}_2\text{O}_3$ layer just below the TiO$_2$ layer [43]. The deformation process of pure titanium occurs through various slip systems and twinning, which improves the formability of the alloys and composite. Table 2.1 compares some of the physical properties of mostly used structural materials along with titanium [44].

Table 2.1: Physical properties of some pure metals used as structural materials [44]

<table>
<thead>
<tr>
<th>Properties</th>
<th>Ti</th>
<th>Al</th>
<th>Mg</th>
<th>Fe</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm$^3$)</td>
<td>4.507</td>
<td>2.698</td>
<td>1.738</td>
<td>7.870</td>
<td>8.902</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>1668</td>
<td>660</td>
<td>650</td>
<td>1538</td>
<td>1453</td>
</tr>
<tr>
<td>Crystal Structure</td>
<td>hcp to bcc (883°C)</td>
<td>fcc</td>
<td>hcp</td>
<td>bcc to fcc (912°C)</td>
<td>fcc</td>
</tr>
<tr>
<td>Yield strength (MPa)</td>
<td>140</td>
<td>30</td>
<td>21</td>
<td>55</td>
<td>59</td>
</tr>
<tr>
<td>Modulus of elasticity (GPa)</td>
<td>115</td>
<td>62</td>
<td>43</td>
<td>208</td>
<td>207</td>
</tr>
<tr>
<td>Coefficient of linear thermal expansion (x10$^{-6}$/°C)</td>
<td>8.41</td>
<td>11</td>
<td>25.2</td>
<td>11.8</td>
<td>13.3</td>
</tr>
<tr>
<td>Oxidation resistance</td>
<td>very low</td>
<td>low</td>
<td>low</td>
<td>high</td>
<td>high</td>
</tr>
<tr>
<td>Corrosion resistance</td>
<td>very high</td>
<td>high</td>
<td>high</td>
<td>low</td>
<td>medium</td>
</tr>
<tr>
<td>Chemical inertness</td>
<td>very high</td>
<td>high</td>
<td>high</td>
<td>low</td>
<td>medium</td>
</tr>
</tbody>
</table>

2.2.2 Phases and Microstructures

The crystal structure of pure titanium changes from a hexagonal closed packed $\alpha$-phase to a body centred cubic $\beta$-phase at a temperature of 882°C. This temperature is called the beta-transus temperature. During processing of titanium alloys and composites at high temperature, the $\alpha$-phase transforms to $\beta$-phase and the $\alpha$-phase nucleates in cooling. The impurity or alloying elements has an influence on this beta-transus temperature. Mainly two different phases are observed in titanium alloys and composites: $\alpha$-phase and $\beta$-phase. Depending on the amount of phases present in the microstructure, the alloy could be $\alpha$, $\beta$ or $\alpha+\beta$. The amount of $\alpha$ and $\beta$ phases depends on the composition of alloying elements. Fig 2.1 schematically represents the effect of various alloying elements on phases of titanium alloys and compounds [43].
2.2.2.1 Alpha Titanium

The microstructure of commercially pure titanium is α-phase. Impurities such as Al, O, N and C increases the beta-transus temperature to a higher temperature called alpha stabilizer. These impurities have large solubility in titanium matrix. Aluminium atoms make substitutional solid solutions while oxygen, nitrogen and carbon atom exist as interstitial solid solution in titanium matrix. Other elements, such as B, Ga, Ge and other rare earth metals are also alpha stabilizers with limited solubility. The maximum solubility of Al in titanium is 6 wt%. Above this content intermetallic compounds Ti₃Al (α₂-phase) and TiAl (γ-phase) appears. Most of the pure titanium contains a small amount of oxygen and Fe as impurities. The amount of alpha stabilizers in titanium are represented in terms of aluminium equivalent [43]:

\[ [\text{Al}]_{\text{eq}} = [\text{Al}] + 0.17[\text{Zr}] + 0.33[\text{Sn}] + 10[\text{O}] \]

2.2.2.2 Beta Titanium

The presence of alloying elements that lower the beta-transus temperature are called beta-stabilizers and the microstructure consists of β-phase. Elements such as Mo, V and Nb are isomorphous type β-stabilizers, which are miscible in the β-phase, whereas Fe, Cr, Mn, Si, Co, Ni, Cu are eutectoid type β-stabilizers that form eutectoids at approximately 333°C below the β-transus temperature. The maximum content of Mo and V in titanium alloys is 15wt% along with 1–3 wt% Nb. Fe content is restricted to 5.5 at% to avoid precipitation of TiFe intermetallic phase [45]. Si is added to improve the high temperature
properties. The amount of beta-stabilizers in titanium alloys is represented as molybdenum equivalent [43]:

$$[\text{Mo}]_{\text{eq}} = [\text{Mo}] + 0.2[\text{Ta}] + 0.28[\text{Nb}] + 0.4[\text{W}] + 0.67[\text{V}] + 1.25[\text{Cr}] + 1.25[\text{Ni}] + 1.7[\text{Mn}] + 1.7[\text{Co}] + 2.5[\text{Fe}]$$

2.2.2.3 Alpha-Beta Titanium

The addition of certain amounts of $\alpha$ and $\beta$ stabilizing elements makes the microstructure a mixture of $\alpha$ and $\beta$ phases, known as ($\alpha+\beta$) titanium. Ti-6Al-4V is a type of alloy that has wide applications both at room and high temperatures. Martensite forms in the microstructure of ($\alpha+\beta$) alloys when it is cooled at a higher rate from beta processing temperatures and widmanstatten or lamellar structure appear at slower cooling rates [45].

2.2.3 Applications

Despite its attractive physical properties, the consumption of titanium is still much lower, compared with other structural materials because of its low benefit-cost ratio. Current titanium products [6, 9, 10, 46] on the market are mostly used in (i) the aerospace industry for frames, landing gear, compressor fan blades (ii) chemical and power industries (iii) offshore drilling equipment that involves reactive salt water (iv) civil engineering associated structures (v) military applications (vi) consumer products and (vii) racing cars. It is expected that a large volume of titanium alloys and composites will be employed in aerospace and automotive sector once its performance overtakes their manufacturing cost.

2.2.4 Manufacturing Techniques

Titanium alloys and composites can be prepared in liquid and solid state processing. Liquid state processing involves melting of materials through a number of techniques, such as stir casting, rheocasting, infiltration, squeeze casting infiltration, gas pressure infiltration, and pressure die infiltration. In liquid state processing, the density and wettability of the matrix and reinforcing materials have to be carefully considered to achieve good microstructural homogeneity and interfacial bonding. Occasionally, coating is performed on these reinforcing agents to improve the wetting properties. On the other hand solid state processing also known as powder metallurgy technique does not require the materials to be melted in the furnace. In this processing technique, the raw materials in powder form are consolidated into bulk materials. The densification of compact occurs
through solid state diffusion of atoms and molecules between the particles during thermal treatment.

2.3 Powder Metallurgy System

Powder metallurgy is the cheapest processing technology for processing of engineered materials. Powder metallurgy processing of titanium alloy composites eliminates the step melting and casting process in vacuum arc remelting (VAR) furnace, which is a complex and expensive operation. Powder metallurgy processing provides certain advantages over cast/ingot processing [47] especially for near net shape manufacturing of complex shapes. Near net shape manufacturing significantly reduces material waste at the machining stage. Titanium parts required for different applications, particularly in aerospace industries, are usually obtained from machining of wrought/ingot materials and forged to achieve desirable mechanical properties. The amount of material used in the final components accounts for 15-20% of total raw materials and the remaining becomes scrap [48], which is difficult to process for recycling by remelting.

Powder metallurgy offers the best option to incorporate light reinforcing elements inside the heavier metals for the preparation of titanium composites. Light reinforcing agents often segregate and float in the melt during the casting process due to density differences, resulting in an inhomogeneous microstructure that affects the mechanical properties. The mechanical properties of the composite greatly depend on the microstructure, hence, the powder metallurgy system gives better control over the microstructure by tailoring fine grains through its processing parameters.

2.3.1 Effect of Raw Powders

Generally, two types of commercially pure titanium (CP-Ti) powders that are available are (i) Sponge fine and (ii) Hydride-dehydride. The high purity of hydride-dehydride powder makes it more expensive than sponge type powders. Recently, titanium hydride (TiH2) powders were introduced in powder metallurgy system for producing alloys and composites. TiH2 powders are more cost effective and easier to compact than CP-Ti powders. The application of TiH2 powder results in more dense compact than commercially pure titanium powders [49] under the same compaction (700 MPa) and sintering conditions (1200°C, 4h). The densification occurs rapidly in the region of α-phase followed by dehydrogenation of the powders. The dehydrogenation process
reduces the oxide layer and enhances the diffusion process despite release of massive hydrogen gas above 600°C remains a concern.

Pure titanium powder usually contains some sort of impurities such as O, N, C, H, Cl, Fe originating from the ores and various stages of the extraction process. The mechanical properties of pure titanium vary on the concentration of these impurities [50]. Fe atoms form substitutional solid solution while O, N and C atoms form interstitial solid solution in these raw powders. The higher content of O and N in the raw powder increases the hardness of the powder thereby reduces the green density [51]. Inclusions such as Cl, Na and Mg have a deleterious effect on densification during compaction and sintering [50].

The size and shape of the initial powder also affects the microstructure and density of the composites via compaction pressure and sintering conditions. A high density in the bulks can be obtained using fine and spherical shaped powders though fine powders have the potential to contain higher amounts of oxygen. Spherical powders are free flowing and possess higher tap density for loading into the die. The distribution of reinforcements and grain sizes are more homogeneous in the composites when spherical shape powders are used. Sponge titanium powders are highly irregular in shape and contains many pores. Thus the tap density of sponge titanium powder can be improved by the milling process until the porosity is reduced by plastic deformation. Performing milling operation of these powders also helps to uniformly distribute inclusions such as NaCl and Fe present in the raw powders. This has the advantage of restraining grain growth by the pinning effect. It also helps to nucleate alpha phase evenly in the matrix during cooling process resulting in fine equiaxed grains [50].

The size ratio of powders, packing density, relative spatial distribution and particle contacts all have a strong influence on the distribution of the reinforcement in the composite. Large differences in powder sizes often involves incomplete reactions between the matrix and reinforcement as a result of insufficient contact for diffusion. Mixing of different sizes of powder help to fill the interstitial spaces between the powders, increasing the tap density. In order to obtain a good packing density the powder sizes ratio should be 20:1 for bimodal powders and 49:7:1 for trimodal powders [52].

2.3.2 Mixing of Powders

Blended elemental (BE) and pre-alloyed types of powder can be used in a powder metallurgy system. In the BE method, elemental Ti powder is mixed with other alloy powders or reinforcements to make the composition, whereas pre-alloyed powders come
from the master alloy. Blended elemental powders are easier to compact than the pre-
alloyed powders [53]. Mixing of the powder is an important step to homogenize its composition. Mixing can be done either manually or by ball milling process. The use of ball milling is the most common and effective method to distribute reinforcements in the matrix uniformly. The operation parameters include milling time, speed, ball to powder weight ratio and sizes of the balls.

2.3.3 Powder Consolidation
Conventional cold pressing and sintering [7] is the simplest and convenient way for mass production of composites. In this method powder mixtures are cold pressed using a die and punch system to obtain green compacts. Titanium is a ductile material and gives good plasticity in the compaction process. The powder particles comes into intimate contact after cold pressing and forms a neck like structure in the green compacts. Lubrication is generally avoided during compaction of powders to keep the product free of contamination in the sintering process. The compaction pressure of titanium powder should give at least more than 80% pore free microstructure in the green compact. A study reveals that parts with green density of 4.2 g/cm³ can be obtained after applying 1400 MPa pressure on commercially pure titanium powders. Cold isostatic pressing gives more uniformity in the green compacts [1] due to simultaneous pressing from various directions. TiH₂ powders are harder than commercially pure titanium powder but give good green density at lower compaction pressure as it breaks down into fine particles [54]. Following the cold pressing of powders, the green compact is sintered at high temperatures for various holding time to obtain sintered composites. During sintering process, the diffusion of atoms and molecules within the particles densify the compact by reducing the neck like pores. The high surface area of the smaller particles gives higher sintered density as the surface diffusion rate is higher during sintering process. The appearance of any transient liquid phase accelerates the densification process further. The presence of oxygen and nitrogen in titanium powders inhibits the diffusion process. Oxygen and nitrogen has a different solubility limit for α-phase and β-phase. The maximum solubility of oxygen and nitrogen in α-Ti is 14.25 at% and 7.6 at%, which is reduced to 2.75 at% and 2.1 at% in the β-phase, respectively [55]. The oxide and nitride layer dissolves at a temperature range above 550-700°C that enhances sintering of the powders [56]. Effective sintering of pure titanium starts at 700°C after the oxide layer disappears. The presence of chlorides is another major obstacle in obtaining a pore free microstructure even after hot forging [1]. Commercially, the sintering operation is
performed in Ar atmosphere and purification of Ar can be done by passing the gas over heated titanium chips first.

However, the most effective way to obtain a highly dense and pore free microstructure of the composite occurs during hot pressing or hot isostatic pressing of the composite powders. Extrusion of powders is also employed for the preparation of many composites with fine grains, or textured microstructures with anisotropic mechanical properties [57]. The advent of spark plasma sintering (SPS) led to its use for manufacturing composites where reaction between matrix and reinforcement is a vital factor. SPS is a novel powder consolidation technique to produce pore free compacts at lower pressure, lower temperature and short processing time. SPS processing of pure Ti powders (45µm) at 950°C (heating rate of 200°C/min) for 5 min under 60 MPa compaction pressure is sufficient to produce fully dense compact even at a low vacuum of 2 Pa [58, 59]. The short processing time significantly lowers the interfacial reaction and oxidation of the composites. Powder injection moulding has also been used to produce various parts in some research [60]. Another new technique is the high temperature self-propagating synthesis (SHS), where chemically evolved energy take parts in the densification process. This can be done by either igniting at a local place or raising the heat at a certain temperature, which in this case is 880°C, the beta-transus temperature of titanium [61].

2.4 Titanium Matrix Composites (TMC)

The microstructure of titanium matrix composite plays a vital role in determining the mechanical properties. Fine and equiaxed microstructure results in enhanced mechanical properties. Microstructures may be comprised of various phases with varying morphology as most of the matrix materials are alloys composed of α and β stabilizers instead of pure Ti. Diffusion data and phase diagram of individual alloying elements helps to understand the nature of phase formation. The size, shape and number of phases can be modified by changing the alloying elements, reinforcing compounds, processing conditions, cooling rate, annealing and aging conditions. Usually hard ceramic compounds are considered as suitable reinforcing agents in soft titanium matrix for high temperature service. These reinforcements can have varying morphology, such as particles, whisker, and nanotubes.
2.4.1 Selection of Reinforcement

The selection of a reinforcing agent is an important step to justify the performance of a composite for room and high temperature practical applications. The performance of a composite is determined on how effectively the load is transferred from the soft matrix material to the hard reinforcing agent. A reinforcing agent with high specific strength and hardness is always preferable. In order to achieve a smooth load transfer, the reinforcement should be uniformly distributed in the matrix. The solubility of the reinforcement must be as low as possible so that it retains its structural integrity in the matrix. The formation of a solid solution by the reinforcement in the matrix would increase its strength but would reduce the malleability and ductility of the composite for further processing.

As most of the metal matrix composite preparation involves high temperature processing, reinforcement with higher oxidation resistance gives an extra advantage. Coefficient of thermal expansion (CTE) of the matrix and reinforcement is another parameter that determines the thermal mismatch between the matrix and the reinforcement during high temperature processing of the composite. A large difference in CTE between matrix and reinforcement causes the retention of residual stress at the interface after processing. This residual stress under load application acts as a stress concentration zone, resulting in abrupt strain in the composite and leading to catastrophic failure.

The reaction between matrix and reinforcement should be as low as possible. A thin layer (<20 nm) of reaction product between the matrix and reinforcement is always beneficial for stable bonding [62], while a thicker layer (>100 nm) is responsible for catastrophic failure of the composite as the reaction phases are unable to bear deformation process by necking and shearing [63]. In the case of the formation of the second phase, its contribution to strength in terms of volume fraction needs to be identified. Spherical and coherent second phases are effective at preventing dislocation movement. Any residual thermal stress may induce preferential localised strain in that region, which may result in unexpected failure before it passes maximum strength. Table 2.2 represents a comparison of physical, mechanical and chemical properties for some of the reinforcing agents currently used in titanium matrix composites [8, 64].
Table 2.2: Properties of some reinforcing compounds currently in use [8, 64]

<table>
<thead>
<tr>
<th>Reinforcing compounds</th>
<th>Melting Point (°C)</th>
<th>Density (g/cm³)</th>
<th>Young’s Modulus (GPa)</th>
<th>Vickers Hardness</th>
<th>Coefficient of Linear Expansion (x10⁶K⁻¹)</th>
<th>Maximum solubility (at%)</th>
<th>Gibbs free Energy at 1000°C (Kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>1668</td>
<td>4.57</td>
<td>110</td>
<td>150</td>
<td>8.60</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TiB</td>
<td>2200</td>
<td>4.56</td>
<td>371</td>
<td>1800</td>
<td>7.15</td>
<td>0.001-1</td>
<td>-35</td>
</tr>
<tr>
<td>TiN</td>
<td>3220</td>
<td>5.43</td>
<td>390</td>
<td>2300</td>
<td>9.35</td>
<td>22-26</td>
<td>-50</td>
</tr>
<tr>
<td>TiC</td>
<td>3054</td>
<td>4.92</td>
<td>460</td>
<td>3200</td>
<td>7.95</td>
<td>1.2-15</td>
<td>-40</td>
</tr>
<tr>
<td>TiB₂</td>
<td>2970</td>
<td>4.52</td>
<td>540</td>
<td>2200</td>
<td>6.20</td>
<td>unstable</td>
<td>-63</td>
</tr>
<tr>
<td>B₄C</td>
<td>-</td>
<td>-</td>
<td>449</td>
<td>-</td>
<td>4.5</td>
<td>unstable</td>
<td>-</td>
</tr>
<tr>
<td>SiC</td>
<td>-</td>
<td>-</td>
<td>420</td>
<td>-</td>
<td>4.3</td>
<td>unstable</td>
<td>-</td>
</tr>
<tr>
<td>Si₃Ni₄</td>
<td>-</td>
<td>-</td>
<td>320</td>
<td>-</td>
<td>3.2</td>
<td>unstable</td>
<td>-</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>-</td>
<td>-</td>
<td>350</td>
<td>-</td>
<td>8.1</td>
<td>unstable</td>
<td>-</td>
</tr>
</tbody>
</table>

2.4.2 Interfacial Reactions

The matrix material often reacts with the reinforcement to form interfacial reaction products at the matrix-reinforcement interface. Such reactions occur at the high temperature stage of processing of the composites. The kind of phase formation depends on the composition and temperature. Reinforcing elements could be dissolved in the matrix to form a solid solution. In other cases, they may react to form various kind of compounds. The analysis of phase diagrams helps to select the composition and temperature during composite preparation.

2.4.3 Types of Reinforcements

Reinforcement can be continuous or discontinuous. In continuous reinforcement, reinforcing agents like SiC and Al₂O₃ fibres are continuously aligned in the matrix, mostly in the form of preform to fabricate composites [65, 66]. These composites are conventional, and involve complex procedures and anisotropic in properties. On the other hand, discontinuous type reinforcements in the form of particles, whiskers, nanorods and
nanotubes (for example B$_4$C, BN, Al$_2$O$_3$, Y$_2$O$_3$, La$_2$O$_3$, Nd$_2$O$_3$, CNT etc) are randomly oriented in the matrix.

However, finding a suitable reinforcement for titanium matrix is always challenging, as most of the reinforcing elements are not chemically stable at high temperature during thermo-mechanical processing of the composites. Therefore, recent trend for designing titanium matrix composites is focused on in-situ formed reinforcements like TiB, TiC, TiN, Si$_3$Ni$_4$, Ti$_5$Si$_3$ and their combinations in titanium matrix [67-71]. In-situ formed reinforcements are advantageous as their formation simultaneously increases the density and strengthens the composite. The lower processing temperature and cost, good distribution and ease in manufacturing are the benefits that can be attained from these in-situ formed discontinuously reinforced composites [72]. The reinforcement of second phase in the matrix also restricts the grain growth during high temperature processing of the composite, resulting in nanocrystalized microstructures. These nanocrystallined grains help to increase the mechanical properties by crack deflection, crack bridging and transforming the cracking mode from transgranular to intergranular [73].

2.4.4 Particle Reinforced Composites

Various types of oxide particles like Al$_2$O$_3$, Y$_2$O$_3$, La$_2$O$_3$, Nd$_2$O$_3$, SiO$_2$, ZrO$_2$ and their combinations are commonly reinforced in Ti matrix now a days [74-78]. Other than these oxide particles BN, Si$_3$N$_4$ and C particles are also used in many research for preparation of titanium matrix composites.

2.4.4.1 Boron Nitride (BN) Particle Reinforced Composite

Boron nitride particles, both in cubic and hexagonal crystal form, possess low density, high hardness, good chemical and thermal stability at high temperatures. Boron nitride particle has an affinity to titanium for making bonds and reactions by forming TiN, TiB$_2$ and TiB compounds as can be seen from their binary phase diagram in Fig 2.2 [55]. The concentration of boron has no effect on beta-transus but titanium reacts with boron to form TiB, as long as the boron concentration is available up to 18.29 wt% (49.87 at%). Above this concentration, it forms Ti$_3$B$_4$ and then TiB$_2$. Therefore, below 882°C, the microstructure is a mixture of α-Ti and TiB, whereas above the transition temperature it is a mixture of β-Ti and TiB. Nitrogen atoms act as an alpha stabilizer that increases beta-transus to a higher temperature. Its concentration from 0.96 wt% to 12.34 wt% gives a
mixture of $\alpha$-Ti and Ti$_2$N phase below 1050°C. On the other hand, above 1050°C, it is a mixture of $\alpha$-Ti and TiN in the concentration range of nitrogen from 8.04 wt% to 11.13 wt%. According to the phase diagrams, it is evident that a boron nitride reinforced titanium composite might have TiB, TiB$_2$, Ti$_2$N and TiN phases present in the microstructure depending on Ti and BN concentrations. At lower BN concentrations, it reacts to Ti forming TiB and TiN phases by the reaction:

$$2\text{Ti} + \text{BN} = \text{TiN} + \text{TiB}$$

A further increase in the BN content reduces the amount of TiB as a result of TiB$_2$ formation by the reaction:

$$3\text{Ti} + 2\text{BN} = 2\text{TiN} + \text{TiB}_2$$

These compounds exhibit high hardness, high fracture toughness and greater resistance to oxidation and corrosion [79]. Thus, the presence of these equilibrium compounds is expected to enhance the wear and fracture properties of titanium matrix composites. The reaction between Ti, B and N system is also exothermic, which leads to the self-propagating high temperature synthesis (SHS)/combustion synthesis of the composite [80-82]. The SHS conditions may start at the concentration range from 5wt%BN to 15wt%BN [83].

The interfacial reaction products between Ti and BN was investigated by sintering the composites (Ti-10vol%BN) at 1000~1200°C for various holding time in vacuum [84-86]. The phase sequence was found to be BN–TiB$_2$–TiB–Ti$_2$N–$\alpha$Ti(N) as shown in Fig. 2.3.
The B rich TiB₂ phase exist next to the BN phase whereas solid solution of N in Ti matrix is dominant at the Ti side. At high temperature, nitrogen is released by the reaction between Ti and BN. This nitrogen diffuses towards titanium to react with it. When the concentration of nitrogen in the reaction zone reaches a critical value, titanium atoms start to diffuse towards the boron nitride side. The process is driven by the dissolution of nitrogen in titanium, i.e. the chemical potential difference between Ti and α-Ti(N) phases. Another investigation [87] at 1000°C, 1400°C and 1600°C revealed the phase sequences as Ti/αTi-αTi/αTi(Ti₂N)-αTi(Ti₂N)/TiB-TiB/ Ti₃B₄-Ti₃B₄/TiB₂-TiB₂/BN.

Cubic boron nitride (c-BN) particles have a very high level of hardness that make them suitable for the preparation of hard materials, such as cutting tools for machining of quenched steel and cast iron. These hard materials are formed using Ti powders that act as the binder [88-92]. In contrast, hexagonal boron nitride (h-BN) particles are mostly reinforced in Ti for the preparation of ceramic matrix composites with superior mechanical properties [36, 37] consisting of TiN and TiB₂ compounds [38-42]. Table 2.5 represents comparison of the mechanical properties obtained in some h-BN/c-BN reinforced Ti composites.

Figure 2.3: Reactions and phase formations between Ti and BN [84]
Table 2.3: Mechanical properties of c-BN/h-BN reinforced composites

<table>
<thead>
<tr>
<th>Composition</th>
<th>Processing conditions</th>
<th>Hv (GPa)</th>
<th>K&lt;sub&gt;IC&lt;/sub&gt; (MPa.m&lt;sup&gt;1/2&lt;/sup&gt;)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>41.2TiH&lt;sub&gt;2&lt;/sub&gt;-13.1BN-45.7TiN</td>
<td>RSPS (80 MPa, 1600°C, 13 min)</td>
<td>18.9~21.3</td>
<td>4.06~6.16</td>
<td>[79]</td>
</tr>
<tr>
<td>75.9TiH&lt;sub&gt;2&lt;/sub&gt;-24.1BN</td>
<td>RSPS (80 MPa, 1600°C, 13 min)</td>
<td>21.0~21.5</td>
<td>4.37~4.80</td>
<td></td>
</tr>
<tr>
<td>73.5TiH&lt;sub&gt;2&lt;/sub&gt;-14.9BN-11.6B</td>
<td>RSPS (80 MPa, 1600°C, 13 min)</td>
<td>22.0~22.7</td>
<td>4.74~5.04</td>
<td></td>
</tr>
<tr>
<td>71.6TiH&lt;sub&gt;2&lt;/sub&gt;-7.4BN-21B</td>
<td>RSPS (80 MPa, 1600°C, 13 min)</td>
<td>24.7</td>
<td>5.16~6.46</td>
<td></td>
</tr>
<tr>
<td>(wt%)</td>
<td></td>
<td>(0.1Kg-f)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti-hBN (molar ratio 3:2)</td>
<td>HPHT (5 GPa, 1300 °C, 5 min)</td>
<td>8.84 (9.8 N)</td>
<td>-</td>
<td>[36]</td>
</tr>
<tr>
<td>Ti-cBN (molar ratio 1:1)</td>
<td>HP (8x10&lt;sup&gt;9&lt;/sup&gt;Pa, 1750°C, 3 min) + Annealing (1400°C, 1h)</td>
<td>44</td>
<td>-</td>
<td>[88]</td>
</tr>
<tr>
<td>TiN-cBN (10vol%)</td>
<td>SPS (100 MPa, 1600 °C, 600 s)</td>
<td>17</td>
<td>-</td>
<td>[92]</td>
</tr>
<tr>
<td>Ti-B&lt;sub&gt;4&lt;/sub&gt;C (molar ratio 4:1)</td>
<td>CIP + SHS (N&lt;sub&gt;2&lt;/sub&gt; gas, 100 MPa)</td>
<td>46 (Hv)</td>
<td>-</td>
<td>[37]</td>
</tr>
<tr>
<td>TiH&lt;sub&gt;2&lt;/sub&gt;-BN-Ni (1wt%)</td>
<td>RHP (30 MPa, 1850 °C, 30 min)</td>
<td>20.5</td>
<td>6.20</td>
<td>[93]</td>
</tr>
<tr>
<td>Ti-BN-Ni (1wt%)</td>
<td>RHP (40 MPa, 1600 °C, 30 min)</td>
<td>24.5</td>
<td>6.53</td>
<td>[94]</td>
</tr>
<tr>
<td>TiN-TiB&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CS (1900 °C, 90 min)</td>
<td>21</td>
<td>4.0</td>
<td>[95]</td>
</tr>
<tr>
<td>Ti-BN (BN/Ti molar ratio 0.11~0.20)</td>
<td>CP (3 MPa) + CS (N&lt;sub&gt;2&lt;/sub&gt; gas, 0.1~10 MPa)</td>
<td>25</td>
<td>5.9</td>
<td>[96]</td>
</tr>
</tbody>
</table>

RSPS=Reactive spark plasma sintering, HP=Hot Pressing, RHP=Reactive hot pressing, HPHT=High pressure high temperature, CIP=Cold isostatic pressing, CP=Cold pressing, SHS=Self propagating high temperature synthesis, CS=Combustion synthesis
2.4.5 In-situ Formed Reinforcing Composites

The in-situ reinforcing compounds are intentionally produced within the composite by the reaction between Ti and reinforcing agents. For example in-situ compounds TiB, TiC, Ti₅Si₃ etc. appear in the composite as a result of reactions between Ti matrix and reinforcing agents like TiB₂, B₄C, SiC [68, 97]. Of these compounds, TiB has drawn considerable interest among researchers as it gives an excellent balance of strength-ductility property relationship along with improvement in fracture toughness, wear and fatigue properties at room and high temperature. The preparation of TiB reinforced composites is thermodynamically favourable, stable and simple. The needle like morphology with high aspect ratio is advantageous in strengthening the composite.

2.4.5.1 In-situ Formed TiB Reinforced Composites

The in-situ formed TiB reinforced Ti composite allowed for the practical application of titanium composites, both at room and high temperature. TiB reinforced titanium alloy composite was first adopted by Toyota Motors Company in 1998 for the manufacture of intake and exhaust valve of engines [8, 98]. Matrix material for intake valves was Ti-6Al-4V alloy, while heat resistance alloy Ti-6Al-4Sn-4Zr-1Nb-1Mo-0.2Si-0.3O was used for the exhaust valve both of which are capable of operating successfully up to 850°C.

The reaction between Ti and B forms three different compounds TiB, Ti₃B₄ and TiB₂ depending on the mass of B. Among these compounds, TiB₂ has a higher melting point and elastic modulus, which might be considered as a strong candidate for the possible reinforcement in titanium composites. However, the interface between Ti and TiB₂ is not stable and congruent like a clean Ti-TiB interface without any intermediate phase [64]. The formation of TiB is the result of a peritectic reaction between titanium rich liquid and TiB₂. TiB is thermodynamically favourable and chemically/mechanically stable even at high temperatures as a result of minimal residual stress associated at the matrix-reinforcement interface. TiB phase also appears in the composite at a lower processing temperature of 900~1100°C offering flexibility in synthesis. The much higher Young’s modulus of TiB, along with similar density and coefficient of thermal expansion (CTE), rendered them more suitable for the reinforcement of titanium than any other compounds [99]. Almost near CTE values for Ti and TiB helps to eliminate residual stress upon cooling. The coefficient of thermal expansion (CTE) of TiB increases almost linearly with temperature up to 10x10⁶/K at 1000°C [64]. In addition, the density of TiB is almost the same as the Ti that enables structural stability of the composite.
The crystal structure of TiB is B27 orthorhombic (a = 6.12 Å, b = 3.06 Å, c = 4.56 Å) having a zig-zag chain of boron atom along the b-direction. Their hexagonal structured cross-section, as shown in Fig 2.4 [64], is mostly bound by (100), (101), (00\(\overline{1}\)) and (\(\overline{1}01\)) planes. Occasionally, some of these surface decomposes into stepped morphology bound by (00\(\overline{1}\)) and (\(\overline{1}01\)) planes turning a variation in the hexagonal cross-section. Axial growth of TiB is six times faster along [010] direction (the needle axis, which has the lowest activation energy for the diffusion path) than the transverse direction leading to independent whiskers. Some interconnected whiskers may form when multiple growths are intercepted by each other. The crystal structure of TiB\(_2\) is C32 hexagonal (a = 3.033 Å, c = 3.23 Å) with alternating stacking of Ti planes and graphite like B networks in c-direction as represented in Fig 2.5 [100].

A study [100] on the growth of TiB and TiB\(_2\) crystal structure revealed that both consist of a trigonal prism stacked in different ways where boron atom lies at the centre surrounded by six Ti atoms (Fig 2.6). B27 crystal structure forms by horizontal stacking of the prism in a columnar array with two of its rectangular faces connected depicting zigzag B chain along the [010] direction i.e. the column. These columns of prisms are connected to each other at the edges forming pipe like structure composed of Ti atoms with a trapezoidal cross-section. In contrast, trigonal prisms are vertically stacked in a close packed manner with alternate planes of Ti and B atom along the c-direction in TiB\(_2\) crystals. The faster growth of TiB along [010] direction bounded by the slowest growing facets forms needle shape, owing to the Ti and B containing planes and their higher density of stronger bonds compared to the alternating stack of Ti and B planes in TiB\(_2\).
The slowest growth along (0001) and \{1\overline{1}00\} and fastest growth along \{11\overline{2}0\} leads the TiB\textsubscript{2} crystal to two dimensional growth into plate like morphology.

Investigation on TiB\textsubscript{x} coated SiC fiber reinforced Ti-6Al-4V composite revealed formation of TiB and TiB\textsubscript{2} at the interface by the diffusion of B atom to the matrix with negligible diffusion of Ti \[100\]. The high concentration of B at the TiB\textsubscript{x} side diffuses towards Ti to form TiB\textsubscript{2} and then TiB at the Ti-TiB\textsubscript{2} interface. The formation of TiB\textsubscript{2} is a transition phase at the boron rich side that disappears at longer annealing periods providing B for further TiB formation. The growth of TiB and TiB\textsubscript{2} obey a parabolic law indicating a diffusion controlled process. The diffusion of the B atom occurs by the vacancy mechanism with a diffusion coefficient 45 times higher in TiB than TiB\textsubscript{2}. The calculated activation energy for TiB and TiB\textsubscript{2} was 190.3 kJ/mol and 187.2 kJ/mol, respectively \[100\].

The size and shape of in-situ formed TiB depends on the volume fraction of TiB in the composite as shown in Fig 2.7 \[101, 102\]. At a low volume fraction (<30\%), individual randomly oriented long needle with high aspect ratio is observed. In a low volume fraction, the particle contact area between Ti and B is larger and forms long whiskers through complete diffusion of B atom. Composites with a medium volume fraction (50-80\%) shows an interconnected and packed colony of TiB needles. At medium volume fraction, a smaller contact area of particles slows down the reaction resulting in backwards diffusion of Ti to B forming TiB. This is also influenced by the slow diffusion

Figure 2.5: Schematic diagram of (a) B27 crystal structures for TiB and (b) C32 crystal structure for TiB\textsubscript{2} \[100\]
of B atoms in a transverse direction rather than the axial direction. Such a reaction forms short secondary TiB whiskers in a clustered form. As the volume fraction becomes higher, secondary TiB whiskers dominates in the composite. Moreover, an inhomogeneous dispersion of particles and fast processing technique of the composite also results in clustered TiB whiskers along with unreacted B particles in the composite [61]. This can be overcome by using mechanical alloying of initial powders for producing homogeneously distributed and intimately contacted composite powders [103]. Besides, the mechanical alloying also introduces structural defects in the powders that enhances diffusion process in high temperature processing without formation of reaction product at the interfaces [104]. Another approach [105] for achieving a complete reaction could be using bi-modal or tri-modal powders. Different sizes of powders help to fill the gap or void spaces between titanium particles for particle intimation and reduce the diffusion path shorter.

Figure 2.6: Construction of TiB and TiB₂ crystal structure from trigonal prism blocks [100]
The strength of the TiB reinforced composite is mainly determined by the aspect ratio of the TiB whisker. The formation of TiB acts as a pinning effect, resisting the growth of grain size. Table 2.6 represents a number of titanium alloys composites according to the volume fraction of TiB and its effect on mechanical properties.

Table 2.4: Comparison of mechanical properties of TiB reinforced Ti composites

<table>
<thead>
<tr>
<th>Matrix (ASTM Grade-4)</th>
<th>TiB (vol %)</th>
<th>Processing Route</th>
<th>E (GPa)</th>
<th>σ_Y (MPa)</th>
<th>UTS (MPa)</th>
<th>El. (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>-</td>
<td>Wrought</td>
<td>110</td>
<td>480</td>
<td>550</td>
<td>15</td>
<td>[106]</td>
</tr>
<tr>
<td>Ti</td>
<td>0</td>
<td>VAR+HS</td>
<td>109</td>
<td>164</td>
<td>179</td>
<td>20.7</td>
<td>[107]</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>VAR(MACS)+HS</td>
<td>121</td>
<td>639</td>
<td>787</td>
<td>12.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>VAR(MACS)+HS</td>
<td>131</td>
<td>706</td>
<td>902</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>VAR(MACS)+HS</td>
<td>139</td>
<td>842</td>
<td>903</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>20</td>
<td>PM</td>
<td>148</td>
<td>-</td>
<td>673</td>
<td>2.5</td>
<td>[108]</td>
</tr>
<tr>
<td>Ti</td>
<td>~40</td>
<td>SHS/PHIP</td>
<td>191.5</td>
<td>-</td>
<td>140</td>
<td>-</td>
<td>[61]</td>
</tr>
<tr>
<td></td>
<td>~50</td>
<td></td>
<td>227</td>
<td>-</td>
<td>224</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>~60</td>
<td></td>
<td>271</td>
<td></td>
<td>280</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 2.7: The appearance of TiB whiskers with respect to volume fraction [101, 102]
<table>
<thead>
<tr>
<th>Material</th>
<th>Treatment</th>
<th>Tensile Strength</th>
<th>Ultimate Tensile Strength</th>
<th>Elongation</th>
<th>Reduction of Area</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>HIP (1350°C)</td>
<td>326</td>
<td>248.8</td>
<td>-70</td>
<td>-</td>
<td>[64]</td>
</tr>
<tr>
<td>Ti-6Al-4V</td>
<td>HIP</td>
<td>110</td>
<td>1035</td>
<td>0</td>
<td>-</td>
<td>[109]</td>
</tr>
<tr>
<td></td>
<td>MA+HIP</td>
<td>136.6</td>
<td>-</td>
<td>10</td>
<td>0.25</td>
<td>[110]</td>
</tr>
<tr>
<td>Ti-6Al-4V</td>
<td>GA+HIP/E</td>
<td>144</td>
<td>1470</td>
<td>11</td>
<td>3.1</td>
<td>[111]</td>
</tr>
<tr>
<td>Ti-6Al-4V</td>
<td>MM+HIP+H+E</td>
<td>145</td>
<td>1018</td>
<td>20</td>
<td></td>
<td>[57]</td>
</tr>
<tr>
<td>Ti-5Al-2.5Fe</td>
<td>PM+HIP</td>
<td>151</td>
<td>1092</td>
<td>15</td>
<td>0.0</td>
<td>[113]</td>
</tr>
<tr>
<td>Ti-6.4Fe-10.3Mo</td>
<td>PM+HIP</td>
<td>163.2</td>
<td>737</td>
<td>34</td>
<td>0.49</td>
<td>[105]</td>
</tr>
<tr>
<td>Ti-22Al-27Nb</td>
<td>PM+HR+H</td>
<td>701</td>
<td>848</td>
<td>0</td>
<td>6.8</td>
<td>[114]</td>
</tr>
<tr>
<td>Ti-4.0Fe-7.3Mo</td>
<td>SPS</td>
<td>132</td>
<td>-</td>
<td>5</td>
<td></td>
<td>[115]</td>
</tr>
<tr>
<td>Ti-6Al-4V</td>
<td>Press and Sinter</td>
<td>108</td>
<td>850</td>
<td>0</td>
<td></td>
<td>[116]</td>
</tr>
<tr>
<td>Ti-6Al-4V</td>
<td>Pressing and Sintering</td>
<td>1290</td>
<td>1290</td>
<td>5</td>
<td></td>
<td>[8]</td>
</tr>
</tbody>
</table>
2.4.6 Nanotube Reinforced Composites

The large aspect ratio and interfacial area of nanotubes acts as an efficient obstacle for dislocation movement in the composite during plastic deformations. Enhanced mechanical properties were obtained in the composites due to one-dimensional fine particle like dispersion strengthening by nanotubes [117]. Relative to other types of reinforcements, like particles and whiskers, nanotubes provide less interparticle distance, which caused the dislocations to pile up around the nanotubes and shear during the deformation process rather than climbing up or circumvent the obstacle through the Orowan mechanism [118]. Although nanotubes are high strength materials and could be useful for application in composites, the difficulty of mixing and lack of homogenous distribution due to agglomerations caused by van der Waals force reduces their potential in composite preparation. With a high concentration of nanotubes, their agglomeration in the matrix works as stress concentrating defects thus degrading the mechanical properties of the composite. Consequently, employing large amounts of nanotubes as reinforcements does not ensure the improvement of final properties of the composite. Uniform distribution of reinforcing nanotubes in the matrix also determines the quality

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature</th>
<th>Vickers</th>
<th>Hardness</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-6Al-4V</td>
<td>Room</td>
<td>0</td>
<td>135</td>
<td>[50]</td>
</tr>
<tr>
<td>Ti-6Al-4V</td>
<td>(500°C)</td>
<td>0</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>Ti-6Al-4V</td>
<td>(500°C)</td>
<td>10</td>
<td>600</td>
<td></td>
</tr>
<tr>
<td>Ti-6Al-2Sn-4Zr-2Mo</td>
<td>Room</td>
<td>0</td>
<td>575</td>
<td></td>
</tr>
<tr>
<td>Ti-6Al-2Sn-4Zr-2Mo</td>
<td>(500°C)</td>
<td>10</td>
<td>725</td>
<td></td>
</tr>
<tr>
<td>Ti-5Al-4V-1Mo-0.2B</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti-4.3Fe-7Mo-1.4Al-1.4V</td>
<td>0</td>
<td>MM+CIP+S+H S</td>
<td>110</td>
<td>1080</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

of the interfacial bonding, thus improving the properties. The powder metallurgy system is more convenient for the effective incorporation of nanotubes in the matrix than the casting process. An agglomeration of nanotubes is still evident in the powder metallurgy process [119, 120] but the segregation is not severe like casting, which is caused by their low density.

2.4.6.1 Carbon Nanotube (CNT) Reinforced Composites

Carbon nanotubes (CNT) are seamless cylindrical forms of graphene sheets [117] with carbon atoms bonded repeatedly in a hexagonal array. The properties of CNT depends on their diameter, length and atomic arrangement of carbon atoms. These tubes are composed of a single sheet or several sheets, known as single wall and multi-walled nanotubes, with a hollow structure in the core. Multi-walled nanotubes are several concentric single wall nanotubes bonded by secondary van der Waals force and can have varying chirality\(^1\). For electrical and electronic properties, the metallic or semiconducting behaviour of the nanotube is greatly influenced by its chirality [121].

Since the discovery of CNT [122], its physical, mechanical and electronic properties have been investigated extensively, with experimental and numerical simulation demonstrating that CNT possess high strength and high elastic modulus. Their high elastic modulus in the order of TPa [123, 124], high thermal stability up to 2800°C in vacuum and high electrical conductivity approximately 1000 times of copper wire [125], along with high stiffness and low density, made them a suitable candidate for the preparation of composite materials. Because of such outstanding mechanical properties, researchers around the world focused on possible applications of CNT as reinforcing agents in the metal matrix composites, while the application of CNT-polymer composite [126-129] still dominates.

A number of methods, such as arc discharge [130, 131], laser ablation [132, 133], chemical vapour deposition [134] and plasma enhanced chemical vapour deposition [135, 136], is employed to synthesize CNT. Arc discharge and laser ablation yields a low volume fraction of nanotubes for composite preparation. The size of the anode for arc discharge and target for laser ablation also limits their operation for continuity. Moreover, the product also needs to be purified in subsequent steps. All these hurdles are overcome by using the chemical vapour deposition method that continuously produces high purity

\(^1\) Chirality is characterized by chiral index \((n,m)\) denoting the length and orientation of them circumferential vector in the hexagonal carbon lattice. Chiral vector and chiral angle of nanotube is determined by the atomic structure or their arrangements.
and good amount of nanotubes from the decomposition of carbon monoxide or hydrocarbon flow gases.

### 2.4.6.1.1 Uniform Distribution of CNT

The properties of metal matrix composites by reinforcing nanotubes still could not be optimised because of a lacking of uniform distribution of nanotubes in the matrix. Minimizing nanotube agglomeration is key to obtaining homogeneous and fine microstructures, delivering enhanced mechanical properties. Conventional ball milling is an effective method to prepare a mixture of powders with good homogeneity. Although CNT is able to withstand a limited compressive stress and buckling [137], excessive ball milling may damage the walls of the nanotube in conjunction with the collapse of the hollow structure.

The mechanical mixing of Ti powder and CNT was optimized for 5 h, based on XRD and TEM analysis to confirm that nanotube structure remains intact [117]. A longer milling time, [138] for example 15 h, was also employed to disperse nanotubes in the matrix. Several researchers [139, 140] used ethanol as the solvent where CNTs were immersed and ultrasonicated to disperse. Metal powders were added in the CNT containing solvent and dried in an oven to prepare CNT coated metal powders. Previous studies showed that CNTs can also be dispersed using polar zwitterionic surfactant solutions via the wet process [141]. The author used 3-(N, N-dimethylstearylammonio) propanesulfonate as the surfactant, which is highly soluble in water and possesses both hydrophobic and hydrophilic groups. The electrostatic interactions occurs at the hydrophilic end, caused by the positive and negative charges at their head groups. This electrostatic interaction overcomes the van der Waals force between the nanotubes for disintegration.

Kondoh et al. [142, 143] dispersed CNT in Ti particles employing this zwitterionic solution. The metal powders were immersed in the CNT-zwitterionic surfactant solutions, ultra-sonicated and dried in an oven at 100°C for 3 h under Ar atmosphere. The surfactant solid remained in the dried powder as a contaminant, which posed a difficulty for the densification process. They evaporates at 500°C and the evolved gas resulted in pores in the composite. The chemical components were removed by hot pressing in a vacuum at 600°C for 1 h under 20 kN loading before the final consolidation process. The heterogeneous coacervation method [144, 145] was also useful to distribute CNT in the Ti powders. In this method, CNT was heated in hydrogen peroxide to impart electronegativity and Ti powder immersed in cetyl trimethyl ammonium bromide solution. 

27
to become electropositive. The solutions were mixed, stirred, dried, and ground to make CNT coated Ti composite powders.

2.4.6.1.2 Mechanical Properties

Kondoh et al. [146] prepared 0.35wt% CNT reinforced Ti composite by spark plasma sintering and a subsequent hot extrusion process from rapidly solidified atomized Ti powders, resulting in fine grains with full density. The CNT was found to survive in the extruded composite, along with in-situ formed TiC particles as evident from XRD analysis and fracture surface observation. Some large TiC particles also appeared originating from the reaction of agglomerated CNT. The short (3 min) preheating at a temperature of 1000 °C was sufficient to synthesize TiC particle in the composite with an estimated 10-20% CNT taking part in the reaction. It was assumed that TiC formed during the SPS process at 800 °C, since the Gibbs free energy (ΔG) for the formation of TiC at 800 °C was -171.3 kJ/mol. Nanotubes are bonded in the titanium matrix through TiC particles and most of the TiC particles are located around the nanotubes due to the reaction between Ti and CNT. The incorporation of CNT in Ti resulted in reduction in grain size (7.4–8.6 μm) and remained constant irrespective of annealing temperature and time [147]. The grain growth was limited as a result of the pinning effect caused by CNT in the matrix. A significant increase in grain size was observed in the extruded pure Ti after annealing at 200 °C for 100 h by the recovery and grain growth process, however, the grain size reduced after annealing at 400 °C for 100 h as a result of recrystallization process by the nucleation of new grains. The pinning effect of nanotubes and TiC particles effectively restrained the grain growth during hot consolidation and the annealing process and caused the formation of twins by stress concentration. The fraction of TiC in the matrix increased with the content of CNT reinforcement but no effect on their sizes was observed by the annealing conditions and CNT content.

Increased mechanical properties were mainly obtained due to dispersion strengthening by CNT and in-situ formed TiC particles, followed by grain refinement and a small effect by the solid solution of C atom in the matrix. The individual contribution to strength by CNT and TiC could not be determined, as the proportion of reacted CNT into TiC was unknown. TiC particles restricted the grain boundary sliding during the deformation process, imparting strength at room and high temperature. It was also found that composites prepared from fine titanium particles exhibited better mechanical properties than composites from sponge titanium [148].
Similar dispersion strengthening by a combination of nanotubes and TiC phase was also observed in 20vol%CNT reinforced composite prepared by hot pressing at 935°C for 2h in vacuum, resulting in fine grain but porous microstructure [117]. Nanotubes used in the composite were synthesized by arc discharge method that contained 60vol%CNT along with graphite particle contaminants. The presence of nanotubes was identified by TEM while TiC formation was confirmed by XRD analysis. It was mentioned that the zig-zag planes \{100\} and arm chair planes \{110\} of nanotubes are highly reactive compared to the basal plane and responsible for the formation of TiC phase in the matrix.

It has been reported that the formation of TiC can only be avoided using a fast processing technique for the preparation of a composite. Conventional heating takes hours to reach the required processing temperature that transforms most of the CNT into TiC by the reaction. Composites reinforced with 4.5wt%CNT synthesized by rapid heating using radio frequency generator from the melt in 30 sec under Ar atmosphere revealed no second phase formation in the matrix [138]. The nanotubes survived successfully, as confirmed from XPS and Raman spectra. XPS indicated the presence of graphitic carbon and radial breathing mode in Raman spectra distinguished radial structure of carbon-carbon bond of nanotubes. The addition of CNT caused grain refinement of the composite imparting higher hardness.

High temperature compressive properties of 3wt%CNT reinforced Ti composite prepared by spark plasma sintering was also evaluated [144]. The composite was sintered at 800, 900 and 1000°C for a much shorter time of 5 min that resulted in almost fully densified with some porous microstructures. The formation of the TiC phase appeared in the composite as determined by XRD, although unreacted CNT was observed in the pores. The short processing time, the prevention of further diffusion of metal atoms nanotube multi-walls by the nanotube multi-walls and the thermodynamically stable cylindrical structure of nanotube consisting of graphitic basal planes inhibited the transformation of CNT into TiC. TiC starts to form in the composite at a sintering temperature of 800°C, which has a deleterious effect on the mechanical properties. The less densified composite sintered at 800°C showed higher compressive strength than that sintered at 1000°C, having higher density, which is a contrast behaviour for composite materials. This was explained by less strengthening effect by TiC phase than the nanotubes.

In order to minimise the reaction between Ti and CNT, intermetallic compounds like Ti$_2$Ni and Ni$_3$Ti were formed in the composite by the addition of nickel powders [145].
Table 2.5: Mechanical properties of CNT reinforced titanium matrix composites

<table>
<thead>
<tr>
<th>Composition</th>
<th>Processing Conditions</th>
<th>Hv</th>
<th>E  (GPa)</th>
<th>UTS (MPa)</th>
<th>YS (MPa)</th>
<th>El. (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>Melt from induction heating at 1677°C</td>
<td>307</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[138]</td>
</tr>
<tr>
<td>Ti-4.5wt%CNT</td>
<td>SPS (800°C, 0.5 h, 41.6 kN, vacuum), Preheating (1000°C, 3 min, Ar), Extrusion (ratio 37, speed 3 mm/s, die temperature 400°C)</td>
<td>261</td>
<td>-</td>
<td>591</td>
<td>472</td>
<td>36.2</td>
<td>[146]</td>
</tr>
<tr>
<td>Ti-0.35wt%CNT</td>
<td>SPS (800°C, 0.5 h, 41.6 kN, vacuum), Preheating (1000°C, 3 min, Ar), Extrusion (ratio 37, speed 3 mm/s, die temperature 400°C), Annealing (200°C, 100 h)</td>
<td>180</td>
<td>(400°C)</td>
<td>170</td>
<td>(400°C)</td>
<td>24</td>
<td>(400°C)</td>
</tr>
<tr>
<td>Ti</td>
<td>SPS (800°C, 0.5 h, 41.6 kN, vacuum), Preheating (1000°C, 3 min, Ar), Extrusion (ratio 37, speed 3 mm/s, die temperature 400°C), Annealing (200°C, 100 h)</td>
<td>221</td>
<td>120</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[117]</td>
</tr>
<tr>
<td>Ti-20vol%CNT</td>
<td>HP (30 MPa, 935°C, 2h, vacuum 7.8x10⁻³ pa)</td>
<td>90</td>
<td>355</td>
<td>50</td>
<td></td>
<td></td>
<td>[145]</td>
</tr>
<tr>
<td>Ti-3wt%CNT</td>
<td>SPS (800°C, 50 MPa, 5 min, 100°C/min)</td>
<td>-</td>
<td>-</td>
<td>140</td>
<td>(600°C)</td>
<td>118</td>
<td>(600°C)</td>
</tr>
<tr>
<td></td>
<td>SPS (900°C, 50 MPa, 5 min, 100°C/min)</td>
<td>-</td>
<td>-</td>
<td>132</td>
<td>(600°C)</td>
<td>118</td>
<td>(600°C)</td>
</tr>
<tr>
<td></td>
<td>SPS (1000 °C, 50 MPa, 5 min, 100 °C/min)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>TiNi-5vol%CNT</td>
<td>HP (980°C, 1 h, 22 MPa)</td>
<td>90</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[145]</td>
</tr>
<tr>
<td></td>
<td>HP (1050°C, 1 h, 22 MPa)</td>
<td>355</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>HP (1120°C, 1 h, 22 MPa)</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

SPS = Spark Plasma Sintering, HP = Hot Pressing
The mixture of Ti, Ni and 5vol%CNT was hot pressed in two stages; first at 900°C for 1 h with very low heating rate (2°C/min) to avoid liquid phase formation and then sintered at 980°C, 1050°C and 1120°C for 25 min above the eutectic and peritectic reaction temperature to have partial melting under a constant pressure of 22 MPa. A small amount of TiC was detected in the composite sintered at 980°C. As the second sintering temperature increased, the liquid phase promoted the diffusion and accelerated the reaction between Ti and CNT, forming TiC. It has been assumed that most of the carbon atoms taking part in the reaction come from the open ends of CNT. Maximum tensile strength and elongation was obtained in the composite sintered at 1050°C due to combined effect of density, TiC and intermetallic phases. The mechanical properties obtained in some CNT reinforced composites are shown in Table 2.10.

### 2.4.6.1.3 Limitations of CNT as the Reinforcement

The lower bending strength of CNT (28.5 GPa) showed that the stiffness of CNT tends to be reduced after buckling because of the formation of structural defects and might result in inferior mechanical properties in the composite [124]. The hollow structure of a nanotube collapses under compressive stresses [137]. Therefore, mixing of nanotube should be conducted with great care, especially in milling conditions. Damage of structure also occurs and the reaction product TiC appears when nanotubes are uncoated or processed at higher temperature or under slow heating [138]. The brittle nature of TiC imparts less strengthening effect in the composite than CNT [144]. The limitations of CNT as reinforcement in Ti composites instigate alternative choice of nanotube like reinforcement which might have similar kind of strength and physical properties or better. Considering these aspect boron nitride nanotube could be a reliable candidate for reinforcing Ti composites.

### 2.5 Boron Nitride Nanotube (BNNT)

The boron nitride nanotube (BNNT) is structurally analogous to the carbon nanotube with wrapped h-BN sheets in the tubular form where the carbon-carbon bonding in CNTs is replaced by alternating boron-nitrogen bonding. It is a ceramic material that can retain its physical properties even at high temperatures. Some carbon containing BNNT’s are also observed in the stoichiometric compositional form of BC2N [149-151] and BC3 [152]. BNNTs possess high elastic modulus and tensile strength, high resistance to oxidation in air at high temperatures and are they better able to withstand deformations [20, 21]. Their high thermal conductivity enhance the density of the bulks due to rapid diffusion of
molecules during consolidation process [153]. The biocompatibility, cell viability and non-cytotoxicity of BNNTs to osteoblasts and macrophages [154], human embryonic kidney [155] and human neuroblastoma [156] is an added advantage for orthopaedic implants and biomedical applications.

### 2.5.1 Advantages of BNNT over CNT

Carbon nanotube has high elastic modulus (~1TPa) and strength (~100 GPa) but oxidizes at a lower temperature of around 500-550°C that limits high temperature applications. The strength and elastic modulus of BNNT is near to the CNT but shows higher oxidation resistance at a temperature range of 900-950°C. The high thermal stability and high chemically inertness of boron nitride nanotube provides an added advantage for reinforcement in metal matrix composites. The morphology of CNT is not straight, rather it is a curly structure that entangles and bundles easily [157]. CNT is much harder to distribute uniformly in the matrix than straight BNNTs. Uneven distribution of CNT in the matrix causes microvoids, pores that serve stress concentrator leading to catastrophic failure of the composite under load [62]. The strong B-N ionic bonding and intra-layer couplings in BNNT facilitates effective load transfer from the matrix to reinforcement [33]. Boron nitride nanotubes are nontoxic in nature compared to CNT that makes it suitable for possible biomedical applications. Some properties of CNT such as electrical are strongly dependent on the tube chirality and diameter and controlling these parameters in synthesizing multiwalled nanotubes is complex [158, 159], whereas BNNT does not show any dependency on the chirality, tube diameter and number of walls [160]. Table 2.8 shows basic property comparison between BNNTs and CNTs for potential reinforcing candidates in titanium matrix composites.

#### Table 2.6: Property comparison between CNT and BNNT

<table>
<thead>
<tr>
<th>Properties</th>
<th>CNT</th>
<th>BNNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>1.3 g/cm³ [161-163]</td>
<td>2.25 g/cm³ [154]</td>
</tr>
<tr>
<td>Elastic modulus</td>
<td>973 GPa [161-163], 1.8 TPa [123], 1.28 TPa [124]</td>
<td>750~1200 GPa [16, 17]</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>&gt;100 GPa [164]</td>
<td>&gt;24 GPa [18]</td>
</tr>
<tr>
<td>Resistance to oxidation</td>
<td>500°C [165], 400°C [19]</td>
<td>950°C [165], 700–900°C [19]</td>
</tr>
<tr>
<td>Melting point</td>
<td>3652°C</td>
<td>3000°C</td>
</tr>
<tr>
<td>CTE</td>
<td>-</td>
<td>( \alpha_a = 0.2 \times 10^{-6} \text{K}^{-1} ) ( \alpha_c = 8.1 \times 10^{-6} \text{K}^{-1} )</td>
</tr>
</tbody>
</table>
The attractive physical and mechanical characteristics of BNNTs over CNT’s recently triggered research on BNNT reinforced composites based on polymer [22-28] and glass [29, 30] matrix. A comparison of interfacial reaction product thickness between Al-BNNT and Al-CNT system revealed that BNNT is much better reinforcement, as it allows for the formation of thinner reaction zone at the interface than carbides forming at Al-CNT interface. Hence, it is expected that the use of boron nitride nanotube in Ti matrix will significantly enhance the mechanical properties. For example, the 4 wt% BNNT (bamboo & cylindrical) reinforced Hydroxyapatite composite prepared by spark plasma sintering (SPS) method [153], yielded an increase in elastic modulus by 120%, hardness by 129%, fracture toughness by 86% and wear resistance by 75% compared to 25% increase in elastic modulus and 92% increase in fracture toughness for 4 wt% CNT reinforced Hydroxyapatite composites fabricated under the same process [166]. The BNNTs survived even after SPS processing at 1373 K and 70 MPa, as confirmed by TEM and h-BN peak in Raman spectrum. The interfacial shear strength was increased by the strong interfacial bonding due to minimal lattice strain thus providing efficient load transfer from the matrix to reinforcement. The preparation of 5 wt% BNNT reinforced PLC (polylactide-polycaprolactone copolymer) composite films [154] also demonstrated similar increase in elastic modulus by 1370% and tensile strength by 109% with an elongation up to 240%. However, in contrast to CNT, BNNTs are sensitive to ball milling, as their resistance to collision is less. For BNNT reinforced hydroxyapatite and polymer composites, the BNNT’s were dispersed in acetone by ultrasonication for 3 h and then mixed with HA nano-rods followed by drying in oven [153, 154].

Despite having these features, BNNT reinforcement in the metal matrix composite is still in early stages, there is a long way to go to realize its potential for metal matrix composites. Only a few numbers of investigations have been done recently for aluminium matrix composites, while no research has been conducted on titanium to date.

2.5.2 Synthesis of BNNT

Many methods have been developed to date to synthesize different type and sizes of boron nitride nanotubes (BNNT), including arc discharge methods [167], laser ablation [168-170], plasma jets [171], thermal heating [172], carbothermal reduction [173], substituting CNT templates [174-180], CVD method [181-193], ball milling and annealing method [194-203]. Among all of these, ball milling and annealing method are recognised as simple and convenient methods for the production of nanotubes. However, none of these
techniques is currently capable of producing large quantity and high-density boron nitride nanotubes for manufacturing of composites.

2.5.2.1 Arc Discharge Method
The first discovery of boron nitride nanotube took place by arc discharge method. Pure multiwalled boron nitride nanotubes, having ~3 nm inner diameter, ~8 nm outer diameter and length of 200 nm, were synthesized using an arc discharge apparatus [167]. Nanotubes consisting of 7~9 walls with interlayer distance of ~3.3 Å were nucleated and grown around tungsten, clustered at the end of nanotubes helping to bond between B-N instead of B-B and N-N. The nanotube grew as the outer layer of BN was pulled away from the inner layer of coating, since the bonding between BN layers is weak. The h-BN sheets became tubular structures by the sp² bonding with B to N ratio of 1.14.

2.5.2.2 Using Catalyst & Precursor in CVD Method
In this method, B₂O₂ generated from the mixture of ball milled or without milled precursors at high temperature is reacted with NH₃ gas to form BNNT’s, which are deposited onto the surface of a substrate. Conical nanorods [192] with 60 nm diameter and 5 μm lengths were synthesized by ball milling B₄C powders for 100 h in N₂ gas and then annealed at 1300 °C for 8 h under N₂ gas in a combustion boat on which an Fe(NO₃)₃ coated silicon wafer was placed. After annealing, conical nanorods were deposited on the surface of the silicon wafer. Similarly, a mixture of ZnO and B powder with a molar ratio of 1.5:1 was ball milled followed by annealing at 1100 °C for 1.5 h to grow nanowires on to the surface of a stainless steel foil substrate [191]. Boron nitride nanowires were obtained from a precursor of BI₃ powders without milling [193], which was loaded in a combustion boat and annealed at 1100 °C for 30 min under NH₃ gas in a tube furnace. The final obtained nanowires were grown on the silicon substrate.

The precursor may also be a mixture of MgO and B powders [186-188] but it was found that the quality and quantity of BNNTs are strictly dependent on the temperature. For example, below 1100 °C, the quality of nanotube is good but the yield is less. With increasing temperature the yield increases but the diameter of nanotube also increases, whereas above 1250 °C only BN flakes are obtained. This technique poses some limitations as the high vapour pressure of Mg at high temperature easily escalates to the tube growth conditions, the formed Mg₂B₂O₅ during reaction makes the precursor inactive and the absence of Mg particle in nanotube indicating not acting as catalyst. Therefore, a mixture of FeO, MgO and B powder was used as the precursor [189], which
facilitates B$_2$O$_2$ vapor and Fe catalyst to react spontaneously with B powder in the presence of NH$_3$ gas at a wide temperature range of 1100~1700 °C for 1 h. The BNNTs obtained were large (~200 mg) with ~50 nm in diameter. Most of the nanotubes are open at the ends though metals of Fe and Mg could be seen in the ends of some nanotubes, which indicated that the growth mechanism was vapour-liquid-solid (VLS) with catalytic performance. Another important feature of this precursor was that it could be reused until the BN boat is completely filled with BNNT’s so that NH$_3$ gas does not react with B$_2$O$_2$.

### 2.5.2.3 Ball Milling & Annealing Method

First reported by Chen et al. [198-200] this process is also known as the mechano-thermal process, as the conversion from particle to nanotube occurs completely in the solid-state process unlike other methods. Ball milling and annealing is not only suitable for producing boron nitride nanotubes but is also proven to produce a variety and wide range of CNT, Zn nanowires and SiC nanowires [204]. During ball milling, the starting B or BN powders become metastable amorphous structures, which contain contaminated nano metal particles from the balls and container that act as catalysts. The ball milling process facilitates nucleation and the annealing process serves to grow the nanotubes.

Several researchers have explained different mechanism of growth models during the annealing process. One of these distinctive mechanisms is the “catalytic capillarity mechanism” [196] as explained for “bamboo” and “skeletal” structured nanotubes. The starting BN powders are ball milled for 140 h at room temperature under N$_2$ gas atmosphere using stainless steel jar and balls. The ball-milled powders are then annealed at 1300°C for 10 h under a continuous N$_2$ gas flow. In this mechanism, the impurities like Fe and Cr nanoparticles originating from balls and container first nucleate during the annealing process. The surrounding BN nanoparticles start to migrate and accumulate on to the metal particles under epitaxy environment, causing the metal particle to lift up so that the leading edge becomes the outside diameter of nanotube and the trailing edge becomes narrow. As the Fe particle grows in all directions and the nanotube grows mostly
by the surface diffusion, the process reaches a critical stage in which the interfacial capillary force causes the precipitate to make a conical void at the trailing end. The first knot is formed when the leading edge of the precipitate meets the outer circumference of the nanotube. The surface tension on the metal particle caused by interfacial capillary force reduces the aperture and makes the conical void slightly capped. Thus, the growth of nanotube occurs repeating a similar formation of “knot” and “capping”, until the end of surface diffusion of BN particles in the annealing process. The schematic of the mechanism is shown in Fig 2.8 [196].

According to the “root growth mechanism” as explained by J. J. Velazquez-Salazar et al [194], the size and growth of nanotubes are completely dependent on the catalyst particles (e.g. Fe, Cr, Ni ), originating from balls and containers. Crystalline h-BN particles are ball milled for 60~72 hrs under Ar atmosphere in a stainless steel jar and annealed at 1100 °C for 4 h in N₂ atmosphere to produce bamboo type BNNTs comprising a series of stacked cones due to dangling bonds. The distribution and stoichiometry of B and N atoms in the nanotubes are good with the bonding of sp² hybridization, as confirmed by elemental mapping and electron energy loss spectrum (EELS). In the ball milling process,
crystalline h-BN becomes amorphous and the metal nanoparticles originating from balls and container are uniformly distributed in the amorphous BN powders. During the annealing process, the amorphous BN reacts and precipitates onto the metallic nanoparticles to be transformed into crystalline again and forms a cone shape layer depending on the size of the metallic nanoparticle. As the layer of precipitation progress, mechanical strain is induced within the layers causing the first cone to slide. With further annealing, the aggregation of nanoparticles occurs to become polycrystalline metallic particles and sliding of the cone shape BN layer continues in the growth mechanism. The final growth and size of the nanotube is influenced by the size of the polycrystalline metallic particles, which has different crystallographic orientation instead of epitaxial crystallographic relationship between Fe particles and (002) planes of h-BN. The adopted schematic diagram is shown in Fig 2.9 [194].

High density and large quantity multiwalled cylindrical and bamboo structured boron nitride nanotubes (BNNT) and nanowires were obtained by ball milling B powders in NH₃ gas for 150 h at a pressure of 300 KPa followed by annealing at different conditions [197]. The ball milled B powders were then mixed with nitrate containing ethanol
solutions and ultrasonicated. The nitrate catalyst was used to assist in the decomposition
of NH₃ gas and enhance the nitriding reaction during annealing. Multiwalled cylindrical
BNNTs with a diameter of 3~15 nm and length of 2~3 μm were produced after annealing
at 1250~1300°C for 5h under NH₃ gas flow rate of 0.1 l/min. By increasing the annealing
time, longer BNNTs can be produced, whilst their diameter can be altered by varying the
annealing temperature. Bamboo structured BNNT’s with 60~80 nm diameter and ~100 μm length was synthesized by annealing the ball milled powder in N₂+15%H₂ gas at 1050~1100°C for 3 h.

Nanowires with a diameter of 50~80 nm were obtained by coating a stainless steel substrate with B solution and then annealing the substrate at 1100°C for 30 min under N₂+15% H₂ gas. The annealing temperature and time could be optimized based on the nitriding reaction determining N to B ratio from EDX analysis [202]. For cylindrical shaped nanotubes, the nitriding reaction was optimized at 1200°C for 8 h. During this nitriding reaction, a large number of (002) BN layer grows, some of which roll up into nanotubes. Since no metal particles could be observed in the cylindrical nanotubes, this indicates that metal particles do not act as a catalyst. Moreover, the lower bonding energy of N-H (314 kJ/mol) than N-N (945.3 kJ/mol) and unstable nature of NH₃ at high temperature easily decomposes it into N₂ and H₂, helping to accelerate the reaction. All of these imply that the growth mechanism for cylindrical nanotubes is controlled by the nitriding reaction rather than the crystal growth mechanism as in the synthesis of BNNTs under N₂ atmosphere. Table 2.12 compares the aspect ratio of nanotubes synthesized in different ball milling and annealing conditions.

2.5.3 BNNT Reinforced Metal Matrix Composites

The employment of BNNTs in metal matrix composites remains a challenge as most of the metal matrix composite preparation involves high temperature processing, which renders strong interfacial reactions or dissolution of nanotubes in the matrix. Recently, some researchers have attempted to incorporate BNNTs in metal matrix composites, especially in aluminium matrix. The high elastic modulus (~1 TPa), strength (~61 GPa), good flexibility, high oxidation resistance (>950°C) and fracture strength properties of boron nitride nanotube attracted researchers for potential application in metal matrix composites.

The first approach was investigated by Patel et al. [35] growing BNNTs in Fe matrix using the one step CVD method, assuming that conventional nanotube-particle mixing, pressing and sintering may damage the structure of BNNTs. In this method, Fe particles and Fe₂B precursor are mixed and annealed at 1100°C for 3 h in the presence of NH₃ gas to grow BNNTs directly into the matrix. Fracture surface and TEM observation showed the presence of bridging BNNTs between Fe particles along with elongated and necked
nanotubes, indicating the load-bearing capacity of BNNTs under deformation. However, lower density and mechanical properties were obtained in the composite, compared to pure Fe, due to the presence of numerous pores. Hardness increased only in the composite with 50% and 100%Fe$_2$B content. This increase in hardness was believed to be because of the nitriding reaction forming iron nitride (Fe$_3$N) and growth of BNNTs. The Fe$_2$B precursor synthesized by the solution method contained a high amount of oxygen and posed difficulty for pressing. Reduction treated Fe$_2$B particles by hydrogen and carbon monoxide even resulted in deteriorated mechanical properties. The stress-strain curve showed irregular patterns between linear to nonlinear progress as reduction of pores occurred along with densification of the composite during the test. Apart from lower mechanical properties, this study presented constraints including the deformation of composites at higher annealing periods, critical control of Fe$_2$B precursor size for optimal BNNT growth, the presence of oxides in the precursor and the suggestion of further isostatic pressing of the composite to reduce the porosity.

In another effort, metal ions such as Al, Ti and Ni were implanted on the surface of nanotubes applying various accelerating voltages in sputtering. High energy accelerating voltage (~30 kV) resulted in metal ions implanted on the surface and inner walls of nanotube, while uniform coating was obtained with medium accelerating voltage (~20 kV). However, degradation of BNNT walls, the loss of boron nitride crystallinity and the presence of metal oxides was a major obstacle in the preparation of functional metal matrix composites. Yamaguchi et al [157] prepared Al coated BNNT nanohybrid composites by magnetron sputtering with varying thickness of 5~200 nm depending on sputtering time. The crystallinity of the nanotube surface remained undamaged in the nanocomposite. In-situ bending and tensile test showed great influence of aluminium coating thickness on their mechanical properties, although there was force limitation in the TEM equipped with AFM and no hot processing of the composite was carried out.

Aluminium ribbon reinforced up to 5 wt% BNNT prepared by melt spinning method [33, 62] showed absence of aluminium boride (AlB$_2$) or nitride (AlN) reaction products as could be seen aluminium carbide (Al$_4$C$_3$) in Al-CNT composites. The strength of the BNNT reinforced Al ribbon was higher than pure Al, however, overall strength values were comparatively lower than the literature suggesting qualitative comparison rather than quantitative comparison. Such decline in property values might be due to the presence of pores, small sample size or possible sliding during the test. When Al-BNNT composite up to 5wt% reinforcement was prepared by spark plasma sintering (SPS) at
high temperature and high pressure torsion (HPT) at room temperature [34], the mechanical properties of the composite were quite different for these processing methods. The hardness values of SPSed composite decreased with BNNT content because of the increased porosity and grain boundary discontinuity. The fracture surface showed poor adhesion and wettability of nanotubes in the aluminium matrix. On the contrary, HPTed composite has higher hardness with BNNT content because of reduced porosity and grain size though nanotubes failed to retain its structural integrity.

Al-5wt%BNNT composite was too brittle in nature to machine for property testing. The nanotubes are located in the grain boundaries and no interfacial product could be detected by XRD in both category of samples. The interfacial reaction between Al and BNNT was investigated by Lahiri et al. [63] confirming appearance of aluminium nitride (AlN) and aluminium boride (AlB₂) at the interface of the composite processed at 650°C for 2h. At high temperature, nitrogen atoms diffuse to Al matrix forming AlN in Al side and Al diffuses towards BNNT side to react with B forming AlB₂. AlN with equiaxed morphology was higher in mass fraction and more spatially distributed than the elongated AlB₂ around the nanotubes. The growth of AlN along the Al matrix side was coherent, which gives less misfit and stable bonding between Al and BNNTs. The reaction mostly occurred at the outer walls of BNNTs leaving inner walls intact. The broken, defected, knot and joint areas are more prone to react compared to the long and clean surface of BNNTs. The size of AlN and AlB₂ was ~7 nm and ~35 nm, respectively, comparatively much smaller in size and less than Al₄C₃, which readily forms in Al-CNT composite irrespective of processing methods.

It is known that thin interfacial product (5~20 nm) helps to make a stable bond between the matrix and reinforcement while thick bonding (>100 nm) represents a weak point during effective load transfer from the matrix to reinforcement causing catastrophic failure. The fabrication of Al-5vol%BNNT composite by spark plasma sintering rendered 50% improvement in compressive strength [31] with good amount of ductility. Cold rolling (75% reduction in thickness) of the composite showed higher hardness and higher deformability. Fracture surface showed survival of BNNTs after SPS and cold rolling. In addition, BNNT bridging, BNNTs like sword in sheath and telescopic structure of BNNTs due to gradual failure of outer walls when load was transferred from matrix to BNNTs were also observed in the fracture surface.
### Table 2.8: Mechanical properties of BNNT reinforced metal matrix composites

<table>
<thead>
<tr>
<th>Composition</th>
<th>Material Synthesis Conditions</th>
<th>Shape and Size of Sample</th>
<th>Young’s Modulus (GPa)</th>
<th>Strength (MPa)</th>
<th>Hardness</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Particle mixing, Pressing and CVD method</td>
<td>Disc shape, (13 mm diameter)</td>
<td>690 (Yield strength)</td>
<td>497-566 (Yield strength)</td>
<td>32 HRC</td>
<td>[35]</td>
</tr>
<tr>
<td>Fe-BNNT</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>48 HRC</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>Cold press (500-550 MPa), Sintering (550°C, 3 h, vacuum 10^-2 torr)</td>
<td>Disc shape (13 mm x 7 mm)</td>
<td>117.4 kg/cm² (Compressive strength)</td>
<td></td>
<td>32 kg/mm²</td>
<td>[32]</td>
</tr>
<tr>
<td>Al-1.5wt%BNNT</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>145 Kg/mm²</td>
<td></td>
</tr>
<tr>
<td>Al-1.5wt%BNNT amino functionalised</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>180 Kg/mm²</td>
<td></td>
</tr>
<tr>
<td>Al-1.5wt%CNT amino functionalised</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>66 Kg/mm²</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>Spark Plasma Sintering (500°C, 60°C/min, 80 MPa, 1 h, vacuum)</td>
<td>Pellets (20 mm x 5 mm)</td>
<td>142 MPa (Compressive strength)</td>
<td>499 MPa</td>
<td></td>
<td>[31]</td>
</tr>
<tr>
<td>Al-5vol%BNNT</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>506 MPa</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>High Pressure Torsion (2.5 GPa, room Temperature)</td>
<td>Disc shape (10 mm x 0.5 mm)</td>
<td>198.69 MPa (Fracture stress)</td>
<td>0.239</td>
<td></td>
<td>[34]</td>
</tr>
<tr>
<td>Al-3wt%BNNT</td>
<td></td>
<td></td>
<td>304.61 MPa (Fracture stress)</td>
<td>0.062</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>Melt spinning (Induction melting, Ar atmosphere)</td>
<td>Ribbon (50 µm thickness and 5 mm wide)</td>
<td>15</td>
<td>60 MPa (Ultimate tensile strength)</td>
<td></td>
<td>[33, 62]</td>
</tr>
<tr>
<td>Al-1wt%BN</td>
<td></td>
<td></td>
<td>-</td>
<td>50 MPa (Ultimate tensile strength)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-1wt%BNNT</td>
<td></td>
<td></td>
<td>-</td>
<td>110 MPa (Ultimate tensile strength)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-3wt%BNNT</td>
<td></td>
<td></td>
<td>35</td>
<td>150 MPa (Ultimate tensile strength)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-BNNT</td>
<td>Magnetron sputtering, Room temperature</td>
<td>20 nm Al coating on BNNT</td>
<td>1470 MPa (Ultimate tensile strength)</td>
<td></td>
<td></td>
<td>[157]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40 nm Al coating on BNNT</td>
<td>360 MPa (Tensile strength)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Conventional pressing and sintering of amino functionalised BNNTs reinforced Al composite [32] resulted in high hardness and high compressive strength of the composite due to reduction in pores and formation of interfacial products AlB₂ and AlN at the
interface. BNNTs were functionalised with an amino group by ball milling in the presence of NH₄HCO₃ to create defects on the BNNT surface so that amino groups make new bonds with the broken B-N bond. This amino functionalization helps to reduce van der Waals force in BNNTs, resulting in uniform distribution of nanotubes in the matrix. Fracture surface shows well-structured BNNTs without any agglomerations, along with broken BNNTs, BNNT bridging, and few nanotubes pull out implying good interfacial bonding between BNNTS and the Al matrix. High resolution TEM showed the existence of a thin transition layer of AlB₂ in the predominant AlB₂ and AlN phases resulting from the reaction between Al and amorphous BN particles at the interface. Table 2.13 presents the improvement of mechanical properties of some BNNT reinforced metal matrix composite to date.

2.6 Summary

The review discusses the preparation of various kinds of titanium alloys and composites through the powder metallurgy route which represents most effective method to incorporate reinforcements in the matrix. It also showed that conventional pressing and sintering method is the simplest and convenient technique for preparation of titanium matrix composites.

While various reinforcements for titanium are still under investigation, the boron nitride nanotube could be a potential reinforcement in titanium matrix composites according to the reinforcement selection criteria as it exhibits better properties compared to other kinds of reinforcement. The limitation on large quantity boron nitride nanotube production for manufacturing composites has been recognised as a challenge.

In order to achieve the maximum benefit from boron nitride nanotube reinforced titanium matrix composites, two major impediments must be overcome. One is uniform distribution of nanotubes in the matrix and the other is maintaining the structural integrity of the nanotube, as well as minimizing any possible defects that may generate in the nanotubes during the processing conditions. Ball milling operation is advantageous to uniformly distribute the reinforcements in the matrix. A gentle ball milling would minimize damage of nanotubes. Prior to ball milling, a short duration ultrasonification would help to break the nanotube agglomerations.
The dependency of mechanical properties of the composites on microstructure, phases and processing conditions needs to be evaluated for optimized performance.
CHAPTER THREE

3 Experimental Techniques

3.1 Introduction
In this chapter, material processing and characterization techniques are described in details.

3.2 Material Processing and Synthesis
3.2.1 Ball Milling
Ball milling is a useful technique in processing of metal powder. This solid-state technique has been widely used to produce powders with solid-solution, nanocrystals and metastable amorphous phases through a combination of mechanical and chemical processes [205]. In ball milling, powders and balls are incorporated in a milling jar which is attached in a motor driven shaft. Hardened stainless steel jar and balls are mostly used for milling but containers and balls made of zirconia are also used if contamination is of great concern. Under milling operation, powders are continuously impacted between the balls and container walls, causing consecutive fracturing and cold welding of powders which reduces particle size, creates fresh surfaces, forms agglomerations and new phases. The main variables of ball milling operation are rotational speed, milling time, ball to powder weight ratio, ball size and gas atmosphere, influencing the quality of final product. Two kinds of ball milling equipment, i.e. planetary and vertical high-energy ball milling machines were used in this research.

3.2.1.1 Vertical High Energy Ball Milling
The vertical high-energy ball milling machine, as shown in Fig 3.1, was employed to produce fine boron powders under ammonia gas for production of BNNTs. Several grams of commercial boron powder and a small amount of ferric nitrate catalyst were loaded in a stainless steel jar along with stainless steel balls. A permanent magnet was mounted at an angle adjacent to the revolving container. Purpose of this magnet is to increase the collision between balls and jar so that high-energy impact could be created. The specific milling conditions [197] are represented in Table 3.1
Table 3.1: Ball milling conditions in vertical high-energy ball milling

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron powder</td>
<td>4 g</td>
</tr>
<tr>
<td>Ferric nitrate</td>
<td>360 mg</td>
</tr>
<tr>
<td>Number of balls</td>
<td>4</td>
</tr>
<tr>
<td>Ball size</td>
<td>25.38 mm</td>
</tr>
<tr>
<td>Each ball weight</td>
<td>66.032 g</td>
</tr>
<tr>
<td>Ammonia gas pressure</td>
<td>200 kPa</td>
</tr>
<tr>
<td>Milling time</td>
<td>150 h</td>
</tr>
<tr>
<td>Milling speed</td>
<td>110 rpm</td>
</tr>
<tr>
<td>Gas</td>
<td>NH₃</td>
</tr>
</tbody>
</table>

**3.2.1.2 Planetary Ball Milling**

The rotational arrangement of planetary milling machine resembles the rotation of a planet system. Fig 3.2 shows schematic and working principle of a planetary milling machine. The whole system is driven by a motor and speed is controlled by a controller. The milling containers are supported by a disc. The supporting disc revolved around the central axis while the containers rotate around their own axis. The rotational direction of disc and containers are in opposite direction that cause grinding of powders between the
balls and container wall by the effect of centrifugal and frictional force. The planetary ball milling machine (Pulverisette-7, Fritsch GmbH) was used to mix titanium powders with the reinforcing boron nitride particles and boron nitride nanotubes in a stainless steel jar using stainless steel balls in Ar atmosphere. In operation, a balance jar must be used to compensate asymmetric weight of the jar with sample. Fig 3.3 shows the picture of ball milling machine, milling jar and balls employed for mixing purpose.

![Figure 3.2: Schematic diagram of planetary ball milling machine](image1)

To manufacture Ti matrix composites, 0~5 vol% BNNTs or BN particles were added to titanium powder, ultrasonicated, dried, blended and finally loaded in the ball milling container for mixing. The content was calculated based on the density of titanium 4.506 g/cm³, boron nitride nanotube 2.25 g/cm³ [154] and hexagonal boron nitride particle 2.34 g/cm³.

![Figure 3.3: Fritsch P-7 milling machine, milling jar and balls used to mix the powders](image2)
g/cm³ [92]. A gentle ball milling operation was performed in order to reduce the structural damage of the fillers. For optimised mixing, various ball milling conditions were tested: ball sizes of 1, 2 and 5 mm, ball to powder weight ratio of 1-5, milling speed of 100-200 rpm, and milling time of 10-20 min. Table 3.2 represents the optimized ball milling conditions for mixing of powders using the planetary milling machine. The optimized conditions gave uniform distribution of boron nitride particles/nanotubes in titanium powders without structural damage. After the mixing process, the balls are separated from the powders by sieving method.

Table 3.2: Optimized milling conditions for homogeneously mixing of powders

<table>
<thead>
<tr>
<th>Ball size</th>
<th>1 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ball to powder ratio</td>
<td>2:1</td>
</tr>
<tr>
<td>Milling speed</td>
<td>100 rpm</td>
</tr>
<tr>
<td>Milling time</td>
<td>20 min</td>
</tr>
<tr>
<td>Gas</td>
<td>Ar</td>
</tr>
</tbody>
</table>

### 3.2.2 Glove Box

Glove box is used to handle material that is sensitive to oxidation or moisture in an inert atmosphere. In this study, a MO-4OM (Vacuum Atmospheres Company, USA) glove box which is equipped with an oxygen analyser (AO-316-C) was used for loading and unloading of highly-reactive ball-milled boron powder under nitrogen atmosphere (Fig 3.4). As ball milled boron is highly reactive to oxygen, the oxygen level in the glove box was always kept under 1 ppm. Regeneration of the glove box is conducted from time to time for purification of catalysis. The flowmeter, blower and pressure controller in the glove box automatically controls nitrogen gas pressure inside when in use. After milling operation is completed, the container is purged with Ar gas several times and inserted into an intermediate chamber, i.e. evacuation chamber. Then, the evacuation chamber was pumped and a pressure gauge ensures its vacuum environment. Next, a one way valve was open to allow nitrogen flow from the main chamber to the evacuation chamber. So that equal gas pressure in the main chamber and evacuation chamber was reached. This allowed transfer of sample from the evacuation chamber to the main chamber.
3.2.3 Sputtering Machine

A sputtering machine (Kao Duen Technology Corporation, Taiwan) was used to prepare Ti coated BNNT nanocomposite by DC sputtering. In the sputtering system, highly energised ion containing plasma was created and controlled by magnetic fields [206]. The desired metal target to be deposited was continuously bombarded by these ions (e.g. Ar). This results in ejection of target atoms from the target material. The released atoms travel towards the substrate and deposited on the substrate. After deposition, they condense and coalescence to form atomically thick layers. Pure titanium in the form of disc with a diameter of 50.8 mm and thickness of 3 mm was used as the target. The synthesized BNNTs were first ultrasonicated in ethanol for proper dispersion in the solvent. The nanotube containing solvent was then dropped on the hot surface of silicon wafer substrate heated in a hot plate and kept it for a while. Once the ethanol was evaporated BNNT dispersed silicon wafer was inserted into the sputtering chamber to deposit titanium thin film. The thickness of coating was controlled by applied power and sputtering time. The Ti coated BNNT nanocomposites were then treated at different temperatures to understand possible reaction between Ti and BNNTs at their interface. Table 3.3 represents the conditions for the sputtering operation.

Figure 3.4: Nitrogen gas filled glove box for handling ball milled powders
Table 3.3: The conditions for sputtering operation

<table>
<thead>
<tr>
<th></th>
<th>Titanium disc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target</td>
<td>Target dimension: 50.8 mm (dia) x 3 mm (thickness)</td>
</tr>
<tr>
<td>Gas used</td>
<td>Ar</td>
</tr>
<tr>
<td>Ar gas pressure</td>
<td>5 m Torr</td>
</tr>
<tr>
<td>Ar gas flow rate</td>
<td>30 sccm</td>
</tr>
<tr>
<td>Chamber vacuum level</td>
<td>10⁻⁶ Torr</td>
</tr>
<tr>
<td>Deposition temperature</td>
<td>Room temperature</td>
</tr>
<tr>
<td>Holder rotation</td>
<td>10 rpm</td>
</tr>
<tr>
<td>Power</td>
<td>100 watt</td>
</tr>
<tr>
<td>Time</td>
<td>600 s</td>
</tr>
</tbody>
</table>

3.2.4 Die and Punch

Conventional cold pressing of powders into pellets require a system of die and punch. The die contains a thorough hole at the centre. The hole diameter depends on the diameter of the pellet. Suitable amounts of powder were poured into the die hole and placed between two pins, one at the bottom and another at the top. The bottom pin is inserted through the bottom of the die hole and the top pin on the top surface of the powder. The

![Figure 3.5: Die and punch arrangement for pressing powder](image)
long cylindrical punch transferred the force to the top pin to consolidate the powder. The die used in this research was split type, as can be seen in Fig 3.5. These were made of heat treated steels (H13) to withstand high temperature and pressure. The parts can be integrated into a whole by means of nut and bolt system.

### 3.2.5 Pressing Machine

The pressing machine (Shop Press, Hafco Metal Master, Australia) was used for consolidation of powder into bulks which is pneumatically operated. The powder mixture

![Shop press machine to consolidate powders](image)

**Figure 3.6**: Shop press machine to consolidate powders

![Schematic of cylindrical compact after pressing the powders](image)

**Figure 3.7**: Schematic of cylindrical compact after pressing the powders
of Ti and h-BN particles/BNNTs of 1.2 g was loaded into the die and pressed uniaxially under a load of 5 metric tons (equivalent to 1.5~1.7 GPa pressure) at room temperature in the pressing machine to fabricate 6 mm (diameter) x 9 mm (length) cylindrical green compacts. Fig 3.6 shows a photo of the pressing machine and Fig 3.7 shows schematic drawing of the dimension of the product after pressing.

### 3.2.6 Rotating Furnace

A purposely-designed rotating furnace was designed to produce large quantities of BNNTs of high density by the annealing of ball milled boron powders. Fig 3.8 shows a schematic diagram of the rotating furnace. The furnace tube used in this research was made of alumina (d=50 mm, l=775 mm) to withstand high temperatures. It has one end closed and can be inserted through the centre of heating element. Another thin alumina tube with 4 mm diameter and equal to the length of furnace tube was used as gas inlet. This thin tube goes inside the furnace tube through the encapment and is extended till the closed end of the large tube so that the reaction gas N₂+15%H₂ can reach the powder. The delivery of gas to the end of the tube accelerates the reaction process for nanotube growth. The encapment contains gas inlet points, gas outlet points and a powder insertion hole that can be sealed once the powder was poured.

![Figure 3.8: Schematic diagram of rotating furnace](image)

The outside metal frame houses the heating elements, motors and limit switches. Encapments are connected with the mounting of the heating element in such a way that the whole system rotates. The furnace can be tilted up to an angle of 45° that makes easier
Figure 3.9: Specially designed rotating furnace

Figure 3.10: Differences in the controller temperature
pouring of ball milled boron powders at high temperature through the powder insertion hole. Once the powder is poured this hole can be sealed so that oxidation of the sample can be prevented. The furnace rotates clockwise and anticlockwise up to an angle of 180°. The rotation can expose the powder even at the bottom to the reaction gas at high temperature. Steel balls could be added to facilitate rolling of powders inside the tube. The whole assembly of the furnace can be seen in Fig 3.9.

The rotating furnace shows temperature surge during heating. It was found that a high heating rate (20°C/min) exceeds the set temperature by about 100°C and stays at that temperature. A lower heating rate like 5°C/min is good to reduce the temperature surge as shown in Fig 3.10.

3.2.6.1 Annealing

Ball milled boron powders were annealed at the rotating furnace for synthesis of boron nitride nanotubes under N₂+15%H₂ gas. Powders are poured at high temperature through the hole when the furnace is tilted at an angle of 45°. For comparison powders were also inserted at room temperature. The annealing was performed at different conditions (temperature, time and gas flow rate) to optimize the production of large quantity and high density BN nanotubes of high aspect ratios. It is known that nanotubes or fibres of high aspect ratios are more effective in reinforcement of composites than shorter ones [31]. The rotation of furnace enhanced the reaction between the ball milled powders and gas for growing nanotubes, compared to the conventional tube furnace. The optimized annealing condition was found to be 1200°C for 3 h. The detailed optimization process has been elaborated in chapter 4.

The rotating furnace was also used for sintering. Sintering of the green compact was performed at a temperature ranging from 800°C to 1200°C for 1~3 hrs in Ar atmosphere with a low heating rate of 5°C/min. The rotating furnace was kept stationary during the sintering process.

Titanium coated boron nitride nanotubes dispersed on silicon wafer was heat treated at temperatures from 500°C to 1200°C for various holding time with a low heating rate (5°C/min) in order to analyse the onset, mechanism and evolution of reaction phases. Heat treatments were conducted in the rotation furnace under Ar atmosphere with the furnace stationary.
3.2.7 Turning Machine

Turning machine was used to process the surfaces of work piece. For compression test, it is necessary to obtain a cylindrical sample with 1.5 aspect ratio. The surface finishing and dimension of the sintered composite was not appropriate for compression test samples. Therefore, sintered composites were machined in a turning machine (Colchester Master 2500) into 4.67 mm (diameter) x 7 mm (length) cylinders with aspect ratio 1.5 for compression test. This aspect ratio ensures uniaxial stress condition near the centre of specimen and prevents buckling and delamination effects [207]. During machining process, the work piece which was held in the jaws of chuck rotated with the spindle and cutting tool was fed along the length or diameter direction. Fig 3.11 shows the arrangement of machining process to prepare compression test sample from the sintered composite samples.

Figure 3.11: (a) Sintered composites (b) machined composites (c) Turning machine and (d) special arrangement for turning operation
3.3 Material Characterization

3.3.1 Sample Preparation

3.3.1.1 Cutting
The fabricated composites were cut into disc shape in Struers Accutom-50 machine using alumina and silicon carbide cutting blades for microstructural and phase analysis. The rotation speed 3000 rpm and feed rate (y-direction) 0.01 mm/s was selected for the harder composites i.e. composites with higher amount of reinforcement.

3.3.1.2 Mounting
The disc shape samples were mounted in polyfast and multifast into 30 mm size using Struers CitoPress-20 machine for optical microscope and scanning electron microscopy observations. Mounted samples were also used to perform Vickers hardness testing of the composites. Polyfast resin (15 ml) was used for the samples to be characterized in scanning electron microscopes. For optical microscopy and hardness test, multifast resin was used for mounting of samples. The first heating cycle was at 80°C for 2 min under 25 bar and second cycle was 180°C for 5 min under 250 bar. The cooling rate was high (2 min).

3.3.1.3 Grinding
Mounted samples were consecutively grinded by 600, 1200 and 4000 grit size emery papers in Struers LaboPol-21 machine. Samples were thoroughly washed and ultrasonicated before going to each step of grinding.

3.3.1.4 Polishing
Grinded samples were polished in Struers Rotopol-21 machine using pure OPS (oxide polishing suspensions) + 30 vol% H₂O₂ solution and polishing pads. OPS solution can produce scratch free and deformation free flat surfaces of the samples. The addition of H₂O₂ helps to quick removal of metal particles from the polished surface. Once polishing completed, the samples were immediately immersed into ethanol and subsequently ultrasonicated, washed in hot waters and dried to remove OPS particles from the polished surface. The polishing parameters are given in Table 3.4.
Table 3.4: Polishing conditions for composite samples

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Force</td>
<td>20 N</td>
</tr>
<tr>
<td>Time</td>
<td>15 min</td>
</tr>
<tr>
<td>RPM</td>
<td>300</td>
</tr>
<tr>
<td>Dosing</td>
<td>Pure OPS + H₂O₂ (30 vol %)</td>
</tr>
</tbody>
</table>

3.3.1.5 Etching

Immersion of the polished metal samples in etchant selectively corroded the microstructural feature that could be visualised in microscopy. The quality of etching largely depends on the holding time. For hexagonal crystal structures like Ti, grain size could be observed in optical microscopy by using polarized light. However, in case of Ti composites etching allowed to identify and observe the morphology of different phases. The Ti composites were etched using Kroll’s reagent to observe the microstructural feature of phases. The solution was prepared from a mixture of 5 ml HF, 10 ml HNO₃ and 85 ml H₂O [208]. The polished surfaces were immersed into the solution for 6 s.

3.3.1.6 Scanning Electron Microscopy Specimen

The morphology and quality of the synthesized BN nanotubes were observed by scanning electron microscopy. BNNTs are ceramic compounds and nonconductive and could have charging effect when they are in interaction with electrons. Therefore, a small amount of nanotubes were dispersed on double sided conductive carbon tape placed on an aluminium stub. The conducting nature of carbon tape minimized the charging effect. SEM samples of Ti coated BNNTs dispersed on silicon wafer were prepared in a similar way. For polished composite samples mounted on polyfast resin, silver paint was used to adhere them on the aluminium stub as it is a good conductor. Fracture samples were screwed in a special holder that can be directly inserted into the SEM chamber.

3.3.1.7 Transmission Electron Microscopy Specimen

3.3.1.7.1 Boron Nitride Nanotubes

Small amount of BNNTs were put in ethanol and bath ultrasonicated for few minutes to disperse nanotubes uniformly in the solvent. One drop of the solution was taken by a pipet and transferred onto a hot copper grid coated by holey carbon to remove the solvent. The grid was kept on the hot plate for a while for evaporation of ethanol.
3.3.1.7.2 Composite Foil

The composites were sliced into 0.4 mm by a Struers Accutom-50 machine. The thickness was further reduced to 120 \( \mu \text{m} \) by grinding using 600 grit and then 1200 grit size emery paper. The grinded sample was ultrasonicated and rinsed in ethanol to remove contaminants followed by punching to have a 3 mm diameter disc suitable for TEM holder. This disc was further polished using 1200 and 4000 paper to reduce thickness into 0.50 \( \mu \text{m} \). The polished foil was ultrasonicated in acetone, rinsed in ethanol, dried and put into precision ion polishing system (PIPS) for ion beam milling to create a hole at the centre of the foil.

3.3.2 X-ray Diffractometry

X-ray diffractometry (XRD) has a wide range of application in identifying crystal structures and phases of materials and minerals. The emitted x-rays are generated from an anode metal target when electrons impact on the target inside the X-ray tube [209]. The generated x-ray is directed on the sample and the diffracted beams are detected by the receiver. Then using the Bragg’s law in equation 3.1, it is possible to determine the \((h,k,l)\) values for planes from inter-planner distance.

\[
\theta = \frac{n\lambda}{2d \sin \theta}
\]

Where, \(\lambda\) is the wavelength of x-ray, \(\theta\) is the angle of incidence and \(d\) is the inter-planner distance. The result is interpreted into the cycle of counts in the form of pattern of peaks.

Table 3.5: XRD performing conditions for various kinds of samples

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltage</td>
<td>40 kV</td>
</tr>
<tr>
<td>Current</td>
<td>30 mA</td>
</tr>
<tr>
<td>Step size</td>
<td>0.05</td>
</tr>
<tr>
<td>Time per step</td>
<td>1</td>
</tr>
<tr>
<td>Spot size</td>
<td>1 mm x 1 mm</td>
</tr>
<tr>
<td>20</td>
<td>10~110°</td>
</tr>
<tr>
<td>Scan type</td>
<td>Point focus</td>
</tr>
<tr>
<td>Radiation</td>
<td>CuK(\alpha)</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.154056 nm</td>
</tr>
</tbody>
</table>

The phases can be identified depending on the peak position comparing the standard database. XRD of powders, nanotubes, Ti coated BNNT nanocomposites and sintered composites in this research was carried out in a PANalytical X’pert Pro MRD XL.
machine and the software X’pert HighScore Plus was used to analyse, identify and match the peaks of phases from ICDD PDF4 database. A low noise base made of silicon was used as the substrate. Table 3.5 represents the XRD conditions in obtaining the patterns from the samples.

3.3.3 Optical Microscopy
Optical microscopy has a low resolution compared to other type of microscopy that makes it suitable only to observe the cross-sectional microstructure and morphology of grains in the composites [210]. An Olympus DP71 optical microscope was used in this research to observe the etched composite samples.

3.3.4 Scanning Electron Microscopy
Scanning electron microscopy (SEM) is used to obtain high resolution image of the samples. In SEM, electron is emitted from the cathode and passed through several electromagnetic lenses and apertures to be incident to the specimen. The system requires high vacuum as it deals with electron. The incident beam penetrates top surface of specimen and creates an interaction volume. The penetration depth is dependent on the accelerating voltage and atomic number of elements. Electron beam penetrates deeper at high voltage and in low atomic number elements. The impact of primary electron on the sample causes to produce secondary electron, backscatter electron, auger electron, x-rays and some of them are absorbed as shown in Fig 3.12. The collection of these electrons by different detectors are converted into electrical signals that forms image of the specimen. Secondary electrons mainly originates from the top portion of the interaction volume and easily escapes from the surface of specimen. Secondary electron detector nearest to the sample capture these electrons and gives highest resolution of image. The backscatter electron comes from the deep of the interaction volume and collected by the backscatter detectors located further away above the samples compared to the much closer SE/In-Lens detectors. It produces image with different contrast based on the atomic number of the elements and thus appropriate for phase identification.

In this research Zeiss Supra 55 VP FEG SEM was used for secondary electron imaging and backscattered electron imaging. A sharp tip of tungsten field emission gun provided the beam source. The imaging mode, accelerating voltage and working distance varied depending on the type of samples as represented in Table 3.6.
Table 3.6: SEM imaging conditions for various kind of samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Imaging Mode</th>
<th>Aperture (μm)</th>
<th>Voltage (kV)</th>
<th>Working Distance (mm)</th>
<th>High Current</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesized boron nitride nanotubes</td>
<td>Secondary Electron</td>
<td>30</td>
<td>2</td>
<td>6</td>
<td>Off</td>
</tr>
<tr>
<td>Extraction of nanotubes</td>
<td>Secondary Electron</td>
<td>30</td>
<td>2</td>
<td>6</td>
<td>Off</td>
</tr>
<tr>
<td>Titanium powders</td>
<td>Secondary Electron</td>
<td>30</td>
<td>10</td>
<td>6</td>
<td>Off</td>
</tr>
<tr>
<td>Composite powder mixtures</td>
<td>Secondary Electron</td>
<td>30</td>
<td>5</td>
<td>6</td>
<td>Off</td>
</tr>
<tr>
<td>Titanium coated boron nitride nanotubes</td>
<td>Secondary Electron + In-Lens</td>
<td>30</td>
<td>2</td>
<td>4~6</td>
<td>Off</td>
</tr>
<tr>
<td>Cross-sectional microstructure of composites</td>
<td>Secondary and Backscattered Electron</td>
<td>30</td>
<td>20</td>
<td>6</td>
<td>On</td>
</tr>
<tr>
<td>Fracture surface of composites</td>
<td>Secondary Electron</td>
<td>30</td>
<td>10</td>
<td>7~8</td>
<td>Off</td>
</tr>
</tbody>
</table>

Secondary electron imaging was performed to observe morphology of the raw powders, distribution of reinforcements (particles/nanotubes) in the powder mixture after mixing, morphology and volume fraction of the synthesized nanotubes, fracture surface of the composites and morphological changes in the heat treated titanium coated BN nanotubes.
In-Lens imaging was mostly performed for titanium coated BN nanotube samples and samples dispersed on the silicon wafer substrates. Backscattered electron imaging was used to observe grain structures and distribution of grains and grain boundaries from the cross-sectional microstructure of composites. SEM observation of composite fracture surfaces were conducted on the samples after fracturing is occurred during the compression test. Composites with low volume fraction reinforcement (0~2 vol%) experienced only ductile type deformation while higher content of reinforcement (3~5 vol%) finally fractured into several parts followed by deformations. The fractured samples were screwed in a special kind of holder keeping the fracture surface up and directly inserted into the SEM chamber for observation.

### 3.3.5 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is an important instrument for high resolution imaging at nanoscales. This equipment requires much higher vacuum than scanning electron microscopes. The emitted beam is transmitted through the sample and image is captured by the digital camera installed at the bottom of the machine. Two types of transmission electron microscope JEOL 2100 FEG and JEOL 2100 LaB6 machines were used in this research. The FEG TEM was used to obtain high resolution electron image, diffraction pattern and energy dispersive x-ray spectroscopy (EDX) from the composite foil samples and Ti coated BNNT nanocomposite samples. The LaB6 machine was used for imaging of BN nanotubes. The accelerating voltage and current for imaging was 200 kV and 106~110 μA, respectively. For all the samples single tilt holder was used and the image was captured by employing gatan digital camera. The structure of as-grown BNNTs, reaction at the matrix-reinforcement interface and distribution of reinforcements/precipitated phases in the composites were determined using TEM. EDX analysis, including elemental mapping, line mapping and point analysis was also performed on the composites.

### 3.3.6 Density

The density of the titanium composites was determined by Archimedes method using the equipment as shown in Fig 3.13.
Sintered composites were weighed in air and water, and the density was calculated using the equation

\[ \rho = \frac{W_a}{W_a - W_W} \times \rho_W \]  

(3.2)

Where \( W_a \) is mass in air, \( W_w \) is mass in water and \( \rho_w \) is the density of water which is considered as 1. The relative density of the sintered composites was calculated by using the theoretical density of pure titanium as 4.506 g/cm\(^3\). At least more than five samples from each preparation condition were used to achieve good accuracy in the density measurement data. The density was finally calculated averaging all the values.

3.3.7 Grain Size

The grain size of the composite was measured by line intercept method [208]. In this method, a number of concentric circles were drawn on the images of cross-sectional microstructure of the composites. The number of intercepts between each circular line and grain boundary was counted. Then the circumference of each circle is divided by the corresponding number of intercepts. Finally they are added to find out the grain size. For accuracy purpose, a number of images were used to calculate the average grain size of the composites.

Figure 3.13: Set-up for density measurement by Archimedes method
3.4 Mechanical Properties Evaluation

3.4.1 Vickers Hardness

Hardness of the composites was evaluated by a Vickers micro hardness tester (Highwood, Model HWDV-7S, TTS Unlimited Inc, Japan) under a load of 0.9807 N and dwell time of 10 s. At least nine readings were taken for each sample at some interval positions around the centre of microstructure like an array of square grid for accuracy purpose and the average of hardness values were presented.

3.4.2 Compression Test

Compression tests of the sintered composites were conducted on the cylindrical samples (4.67 mm x 7 mm) in an Instron 8801 machine (100 kN) at room-temperature and 500°C at a cross head speed of 0.005 mm/s. It is a twin-column servo-hydraulic operated machine equipped with video extensometer, hydraulic grips, load cell of 100 kN and environmental chamber. The environmental chamber facilitates to conduct test at a high temperature up to 600°C. Fig 3.14 and Fig 3.15 show the room-temperature and high temperature test arrangement, respectively. For controlling the temperature precisely in the high temperature compression tests, an OMRON E5CK temperature controller was used. The software “Bluehill” was used for compression test of composite samples. Minimum three composite samples for each condition were tested both at room and high temperatures for accurate results and the average values were reported.

![Figure 3.14: Arrangement of room temperature compression test](image-url)
Figure 3.15: Arrangement of high temperature compression test
4 Synthesis of Large Quantity and High Density Boron Nitride Nanotubes

4.1 Introduction

Boron nitride nanotubes (BNNTs) have recently drawn attention of many researchers around the world due to their excellent physical, mechanical and chemical properties comparable to carbon nanotubes [211]. BNNT has high elastic modulus of 750~1200 GPa [16, 17] and tensile strength of about 24 GPa [18]. The in-situ buckling test of multiwalled BNNTs revealed rippled elastic deformation and high fracture strain [212] despite having partially ionic bonding between boron and nitrogen atoms. In-situ bending test showed a bending strength of 100~260 MPa and bending angle of 115° before its failure. The torsional resilience of BNNTs is one order of magnitude higher than that of carbon nanotubes [213]. The strong coupling between the adjacent layers arising from polar nature of B-N bonding causes all the layers together contributing in mechanical stiffness. These attractive properties along with high melting temperature of around 3000°C, high oxidation resistance at the temperature range of 700~950°C, and good thermal and chemical stability [19, 165] make them a suitable candidate for reinforcement filler in composite materials.

For the synthesis of BNNTs, several methods have been established including arc discharge methods [167], laser ablation [168-170], plasma jets [171], thermal heating [172], carbothermal reduction [173], substituting carbon nanotube templates [174-180], chemical vapour deposition method [181-193], and ball milling and annealing method [194-203]. Various types of nanotube structures from cylindrical to bamboo structure [197], single-wall to multiwalled nanotubes, short to long nanotubes (till 1 mm) [201], thinner to coarser diameter nanotube/nanowire/nanorod [191, 192] can be produced via the above mentioned techniques depending on raw materials, reaction gas and processing conditions. However, the low production yield is common issue in all these techniques. Among them, ball milling and annealing method first reported by Chen et al. [214, 215] is known the best technique to produce larger quantities of nanotubes to date. The nanotube yield produced in this method is useful for laboratory research purposes but not
sufficient for manufacturing of composite materials that require large volume of BNNT materials. Besides, the production yield in ball milling and annealing method is also limited by the conventional annealing process of ball milled powder conducted in a horizontal tube furnace. The nanotubes grow only on the top surface of the milled B powders as they meet the nitrogen gas; while the bottom layer of the B powder remains unreacted because of lack of the gas.

Recently Cumings et al. produced high yield of double walled BNNTs in the form of bundles or ropes using plasma-arc method [216] but the samples contained boron nitride coated nanosized boron particles. Also the nanotube quantity was not reported and the bundles and rope tubes are not suitable for production of composite materials. In another research [189] a large quantity multiwalled nanotubes up to ~200 mg were produced in a single run from the precursor of B, FeO and MgO mixture under ammonia gas at annealing temperatures 1100~1700°C for 1 h. But this CVD process is not convenient as it involves precursors and the yield is dependent on higher annealing temperatures. Moreover, the optimized annealing condition for achieving high density, high quality and large quantity nanotube is also not mentioned.

Therefore, synthesis of large quantity and high density of BNNTs remains a prerequisite condition for large scale production of BNNT reinforced metal matrix composites. To overcome this hurdle, a special type of tube furnace known as “rotating furnace” was designed in this research. The effects of various annealing conditions (temperature, time and gas flow rate) on the resulting nanotube sizes, shapes, aspect ratio and yield have been investigated and optimization of annealing conditions for producing large quantity and high density BNNTs has been achieved.

4.2 Experimental

Amorphous boron powder (95-97%, Fluka, Sigma-Aldrich Company) of 4 g and ferric nitrate catalyst (98% purity, M&B) of 360 mg were loaded into a stainless steel jar. Four hardened steel balls with ball to powder weight ratio 264:1 was used in the milling operation. The container was purged with Ar gas for several times followed by filling with NH₃ gas at a pressure of 200 kPa. Ball milling was conducted in a vertical high energy ball milling machine (Fig 3.1) for 150 h at a rotational speed of 110 rpm. After ball milling, the milling container was again purged with Ar gas and the milled boron powder was collected from the milling jar inside nitrogen-filled glove box to prevent
oxidation. Annealing of the milled powder was performed in the specially designed rotating furnace under N\textsubscript{2}-15\%H\textsubscript{2} atmosphere for various conditions from 1000°C to 1300°C for 1 to 6 hrs with a gas flow rate from 0.2 l/min to 4 l/min. The details of rotating furnace and its working principle has already been described in Chapter 3 of “Experimental Techniques”. Ball milled boron powders were placed in the furnace at room temperature or high temperatures and the powder quantity for each run was kept in the range of 200–300 mg. Chrome steel balls with 2 mm diameter were also incorporated in the ball milled powders at a ball to powder ratio of 4:1 to facilitate rolling of the powders during the rotation of the furnace. X-ray diffractometry (XRD) of the as synthesized nanotubes were conducted in a X-pert Pro MRD XL machine using CuK\textsubscript{α} radiation in a 2θ range from 10–110° applying a voltage of 40 kV and current 30 mA. The synthesized BNNTs were observed using a Zeiss Supra 55 VP scanning electron microscope (SEM).

4.3 Results and Discussion

4.3.1 Conventional Nanotube Synthesis

In conventional ball milling and annealing method, the annealing of ball milled boron powder is performed in a horizontal tube furnace. The milled powder is loaded on a crucible or steel plates and inserted into the furnace at high temperature. The reaction gas N\textsubscript{2}+15\%H\textsubscript{2} enters through one side of the quartz tube with a flow rate of 0.2 l/min and exits through the other side. The annealing condition in the horizontal tube furnace was optimized as 1100°C for 3 h for high density nanotube synthesis [197].

Figure 4.1: BNNTs synthesized with the horizontal tube furnace; (a) low magnification and (b) high magnification
Fig. 4.1 shows the image of synthesized nanotubes in such procedure. Nanotubes with few micron meters in length and 50~70 nm diameter were obtained using this conventional tube furnace. The synthesized nanotubes are high in density but not in a large quantity. XRD pattern of the nanotubes (Fig 4.2) exhibits diffraction peaks of BN indicating that the ball milled boron powder has been transformed to boron nitride phase after the reaction. A number of peaks from iron (might be a boride compounds Fe$_{2.12}$B$_{103.36}$) also appear in the pattern [202]. These Fe contaminants mainly come from the milling balls and containers [214]. However, a detailed observation reveals that the nitriding reaction was not uniform as evidence of particles can be observed beneath the nanotubes as shown in Fig 4.3. The particles underneath the nanotube was unable to grow because they could not meet the reaction gas sufficiently and becomes nitrides. During ball milling, the initial boron powder transforms into nanocrystalline structure with homogeneously distributed ferric nitrate catalyst particles within it. And in the annealing process, these nanocrystalline boron particles react with N$_2$ gas to form BN which is deposited onto the metal particles originated from the catalysts, steel balls and jars. The type of reaction gas has influence on the kind and growth of nanotubes [217]. A comparison of different gases N$_2$, N$_2$-5%H$_2$, N$_2$-15%H$_2$ and NH$_3$ shows that as the hydrogen content in the reaction gas
increases, the nitriding reaction during annealing slows down because of the lower partial pressure of nitrogen gas contributed by the hydrogen gas. The faster nitriding reaction by N₂ and N₂-H₂ mixture gases are responsible to produce a mixture of bamboo and cylindrical structured nanotubes with thick and thin diameters.

4.3.2 Nanotube Synthesis with Rotating Furnace

Under the same ball milling and annealing conditions (1100°C, 3h), BNNTs were also synthesized in the newly designed rotating furnace after placing the ball milled powders at room temperature inside the furnace tube. High density nanotubes with similar length and diameter as obtained in the conventional tube furnace also grew in the rotating furnace.

![Figure 4.3: Sintered BN particles underneath the synthesized nanotubes](image)

![Figure 4.4: Boron nitride nanotubes from rotating furnace annealed at 1100°C for 3 h; (a) low magnification and (b) high magnification](image)
furnace as shown in Fig 4.4. The XRD traces obtained from the nanotube showed same position of main peak for hexagonal boron nitride phase confirming occurrence of reaction as can be seen from Fig 4.5. Ball milling and annealing method synthesize nanotube through solid state nucleation and growth process [215]. Ball milling of boron powder in ammonia results in formation of nanocrystalline particles including some portion of disordered boron nitride phase by nitriding reaction. This metastable boron nitride phase acts as a seed for growing nanotubes during annealing. The (002) basal planes of boron nitride phase start to grow at high temperatures which in turn form into tubular structure [196]. The growth thickness is dependent on the specific annealing temperature. Dispersed catalytic particles like Fe, Ni and Cr helps to grow nanotubes and exist at the tip of nanotubes. The size of the catalyst particle at the tip of nanotube determines the outer diameter of the bamboo structure nanotubes and the inner diameter is related to the projected width of the particle’s edge [196, 218]. Observation of as-synthesized nanotubes from rotating furnace under SEM reveals a number of different features: (i) the grown nanotubes are not highly dense like those obtained from conventional tube furnace (ii) the synthesis of nanotube is not uniform in all places and (iii) formation of large spherical particles through agglomeration of smaller nanoparticles.

![Figure 4.5: XRD pattern of BNNTs synthesized with rotating furnace at 1100°C for 3 h](image)

70
It can be assumed that while the furnace is in rotation, the ball milled particles start to form agglomerations as a result of rolling effect though they are not big sizes initially. By the time when the temperature reaches at 1100°C, BNNTs start to grow on these agglomerates. As the particles inside the furnace is rolling, the growing nanotubes entangles to each other as it grows and forms spherical morphology into large particles (Fig 4.6a). In some region, the formation of these large spherical could also be seen without any growing of nanotubes as shown in Fig 4.6b which might happened because of the insufficient catalysts or inappropriate annealing conditions (either temperature or time) resulting in less yield of nanotubes. Therefore, it seems that the annealing condition is needed to be optimized in the rotating furnace as its operation involves rotation of the furnace.

4.3.2.1 Optimizing Annealing Conditions

In order to optimize the annealing conditions, the ball milled boron powders were annealed in a temperature range from 1100°C to 1300°C from 1 to 6 hrs under N₂+15%H₂ gas atmosphere with a flow rate of 0.2 l/min. In all the conditions powders were inserted at room temperature. Fig 4.7 represents XRD pattern obtained from the as synthesized nanotubes. The presence of BN peaks in the XRD pattern indicates nitriding reaction took place between the ball milled powders and reaction gas. The yield and morphology of the synthesized nanotubes obtained from various annealing condition were investigated by using SEM image as demonstrated in Fig 4.8. As can be seen, among all the annealing conditions, a large quantity and high density nanotube was obtained after annealing at 1200 °C for 3 h. The nanotubes are also long which would be effective for reinforcement of composites. Medium yield of nanotube was synthesised in the annealing condition of

Figure 4.6: Formation of agglomerations in the form of large spherical particles; (a) with nanotubes (b) without nanotubes
1100°C for 6 h along with presence of numerous particles. As the annealing temperature and holding time goes up, the size of nanotube becomes coarser and shorter. Annealing at 1200°C for 5 h produce medium density nanotubes most of which are a bit coarser. On the other hand, short and thick whisker like nanotubes along with sintered nanoparticles were observed after annealing at 1300°C for 1 h. Increasing the nanotube diameter with the higher annealing temperature is in agreement with the previous study [214]. Nanotube diameter increased from 25~50 nm to 50~150 nm when annealing temperature increased from 1000°C to 1300°C for a holding time of 6 h in both cases. The dependence of nanotube yield and quality on the annealing temperature is also found in other studies [186] where an increase in the yield but coarser nanotubes were obtained above 1100°C annealing temperature. For reinforcement in composites, nanotubes with high aspect ratio is desirable as it effectively transfers the load from the matrix to the reinforcement. Defect free nanotube also minimizes reaction between the matrix and reinforcement [31]. Therefore, it can be concluded that the optimized annealing condition of 1200 °C for 3 h is the most effective condition for obtaining high yield of long and particle free nanotubes in the rotating furnace. This optimization of annealing condition was carried out while powders were placed at room temperature inside the furnace tube and using a reaction gas flow rate of 0.2 l/min.

Figure 4.7: XRD patterns obtained from nanotubes synthesized at (a) 1100°C for 6 h
Figure 4.8: SEM images of nanotube synthesized under various annealing temperatures and time; (a, b) 1100 °C, 6 h (c, d) 1200°C, 3h (e, f) 1200 °C, 5h (g, h) 1300 °C, 1 h
4.3.2.2 Further Improvement of Nanotube Yield

As mentioned earlier, previous study on the growth of nanotube revealed that the initiation of effective nanotube growth starts within the first few minutes and the growth is faster at the exposure of high temperature. Consequently, the ball milled powders were introduced in the rotating furnace at high temperature i.e. annealing temperature 1200°C instead of placing the powders at room temperature. This was done by pouring powders through the powder insertion hole when the furnace temperature is near to 1200°C. The furnace was tilted at an angle of 45° to ease dropping of powders and returned to the horizontal position after its completion. Another attempt was to add chrome steel balls to the ball milled powders to facilitate more efficient rolling of the powders during annealing. The efficient rolling of the ball milled powders helps to expose them to the reaction gas evenly for better growth of nanotubes. XRD patterns recorded from the as synthesized boron nitride nanotubes (as shown in Fig 4.9) exhibit identical boron nitride peaks as expected. A slight increase in the Fe peaks appears in the samples where steel balls were used. This happened as the excess Fe particles are provided by the steel balls.

Figure 4.9: XRD pattern of the nanotubes synthesized under optimized annealing condition of 1200 °C for 3 h; B powders are inserted at (a) room temperature (b) 1200°C and (c) room temperature with steel balls
The corresponding morphology of the nanotubes are exhibited in Fig 4.10. A good amount of high density long nanotubes were obtained when the powders were inserted at 1200°C. The density and quantity of the nanotubes are even higher when powders were introduced at 1200°C along with steel balls. But the resulting nanotube becomes coarser and shorter. Such kind of highly dense coarse nanotube might be grown due to presence of higher amount of metal particles migrated from the steel balls. This also results in a larger size of metal particle grown in the annealing period producing coarser nanotubes.

The effect of catalyst particles on the formation of nanotubes during annealing was explained by the catalytic capillary mechanism [196]. The nucleation, growth and
propagation of catalyst particles by interfacial capillary along with simultaneous surface diffusion of BN particles leads to the growth of nanotubes. Therefore, the outside diameter of nanotube is controlled by the growth of catalyst particles. However, the steel balls were found to stuck together because of partial melting indicating that the steel balls are not stable at this high temperature.

4.3.2.3 Effect of Gas Flow Rate
While the furnace is in rotation, the rolling of powders continuously changes the powder surface exposure to the reaction gas. As the annealing operation proceeds some powder below the top surface is prevented to take part in the reaction for growing nanotubes. It is therefore assumed that if the powders could be blown simultaneous to the rolling, the reaction would be more homogeneous. Based on this concept the annealing of powders was carried out at 1200°C for 1 h with gas flow rate

![XRD traces of the nanotubes obtained at 1200°C for 1 h with gas flow rate](image)

Figure 4.11: XRD traces of the nanotubes obtained at 1200°C for 1 h with gas flow rate

was carried out at 1200°C for 1 h under N₂+5%H₂ gas atmosphere keeping the furnace tilted at 45°. A gas flow rate of 2 l/min and 4 l/min was applied because much higher gas flow was required for effective blowing of powders. The short duration of annealing was sufficient to convert boron particles to the boron nitride phases according to the XRD
traces shown in Fig 4.11. The synthesized nanotubes obtained in corresponding annealing conditions with different gas flow rates are shown in Fig 4.12. High resolution SEM image displays synthesis of large quantity and highly dense nanotubes even much higher than the optimized annealing conditions (1200°C, 3 h, and 0.2 l/min). Nanotubes synthesized under 2 l/min gas flow (Fig 4.12b) contains a good amount of small particles compared to the nanotubes synthesized under a flow rate of 4 l/min (Fig 4.12d). This can be explained by the fact that the conversion reaction of particles to the nanotube could not take place completely as annealing period was less. However, higher amount of gas flow rate like 4 l/min along with rotation of furnace caused suspension and continuous agitation of powders inside the tube changing powder exposure to the reaction gas. This condition of homogeneous reaction favoured the growth of nanotube spontaneously into very high density. Table 4.1 summarises the findings of various annealing conditions on the finally obtained nanotubes.
### Table 4.1: Effect of processing conditions on the synthesized boron nitride nanotubes

<table>
<thead>
<tr>
<th>Furnace Type</th>
<th>Annealing Condition</th>
<th>Powders Insertion Conditions</th>
<th>Condition of Annealed Powder</th>
<th>Nanotube Size</th>
<th>Nanotube Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional tube furnace</td>
<td>1100°C, 3h, N₂+15%H₂, 0.2 l/min</td>
<td>1100°C</td>
<td>Top surface is nanotube and particles in the beneath</td>
<td>l = 5~7 µm</td>
<td>Density: high</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>d = 50~70 nm</td>
<td>Quantity: low</td>
</tr>
<tr>
<td>Rotating furnace</td>
<td>1200°C, 3h, N₂+15%H₂, 0.2 l/min</td>
<td>Room temperature</td>
<td>Agglomeration size: ~50 µm</td>
<td>l = ~6 µm</td>
<td>Density: high</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>d = 40~50 nm</td>
<td>Quantity: medium</td>
</tr>
<tr>
<td></td>
<td>1200°C</td>
<td></td>
<td>Agglomeration size: ~100 µm</td>
<td>l = ~5 µm</td>
<td>Density: high</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>d = ~90 nm</td>
<td>Quantity: large</td>
</tr>
<tr>
<td></td>
<td>Room temperature + Steel balls</td>
<td></td>
<td>Steel balls partially melted</td>
<td>l = ~2µm</td>
<td>Density: high</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>d = ~100 nm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1200°C + Steel balls</td>
<td>Partial melting of steel balls</td>
<td></td>
<td>l = ~2 µm</td>
<td>Density: very high</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>d = ~100 nm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1200°C, 1h, N₂+5%H₂, 2 l/min</td>
<td>1200°C</td>
<td>Homogeneous nanotube</td>
<td>l = ~1 µm</td>
<td>Density: very high</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>d = ~60 nm</td>
<td>Quantity: very high</td>
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<td>Powder Used: 300 mg</td>
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<td>Nanotube Yield: 260~320 mg</td>
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<td></td>
<td>1200°C, 1h, N₂+5%H₂, 4 l/min</td>
<td>1200°C</td>
<td>Homogeneous nanotube</td>
<td>l = 2~3 µm</td>
<td>Density: very high</td>
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<td></td>
<td>d = 90~140 nm</td>
<td>Quantity: very high</td>
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<td>Powder Used: 300 mg</td>
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<td>Nanotube Yield: 510 mg</td>
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#### 4.3.2.4 Nanotube Yield

Usually most of the current BNNT synthesis method includes ball milling and annealing method and chemical vapour deposition (CVD) method as these are convenient and doesn’t require special equipments. Due to lack of designing capabilities all of them produce small scale of different type nanotube synthesis. These nanotubes are high quality but grow preferentially in the top of powder surface only, while underneath the unreacted boron powder remains. In this research, the rotation of furnace tube enables the powders come into contact with the reaction gas. It makes growing of nanotube more uniformly and larger quantity than other techniques. However, rolling of powder causes formation of agglomeration that restricts the reaction gas to reach inside of agglomerated powders preventing full scale growing of nanotubes. Thus the nanotubes are mostly grown on the surface of agglomerations while the inner side consist of particles. Therefore, it was found that blowing of ball milled boron powders using high gas flow rate while under rotation gives the highest production and good quality BNNTs. The high gas flow rate caused the ball milled powders in suspension while annealing and
Table 4.2: Comparison of nanotube yield through various methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Processing Conditions</th>
<th>Nanotube Yield</th>
<th>Ref.</th>
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</table>
| Ball milling and annealing method – rotating furnace | Annealing at 1200°C for 3 h  
Powder inserted at 1200°C  
Powder used 300 mg  
Gas used (N₂ + 15% H₂)  
Gas flow rate 0.2 l/min | 210–240 mg  
Bamboo type BNNT | This research |
|                                                  | Annealing at 1200°C for 1 h  
Powder inserted at 1200°C  
Powder used 300 mg  
Gas used (N₂ + 5% H₂)  
Gas flow rate 4 l/min  
Powders are suspended while annealing | 510 mg  
Bamboo type BNNT |              |
| Chemical vapour deposition (CVD)                  | Precursor (FeO + MgO + B) powder  
Annealing temperature 1100–1700°C  
Yield is high at high temperature | 200 mg  
Cylindrical type BNNT | [189]        |
| Laser ablation – pressurized vapour/condenser method | Laser capacity 1 kW  
Hot pressed BN target used  
Weight loss of target 80% | 200 mg  
100 mg/h  
Cylindrical type BNNT | [219]        |
| Plasma method                                    | Carrier gas N₂ flow rate 2–5 l/min  
Plasma gas N₂ flow rate 50 l/min  
Power 40–50 kW | 35 g/h  
Cylindrical type BNNT | [220]        |

prevented agglomerations. Another obstacle using rotating furnace was a good amount of powders are stuck on the surface of alumina tube when they are poured through the powder insertion hole. The sticking of powders can be avoided if the furnace tube can be tilted by 90° upwards. According to the current design, the furnace is able to be tilted up to 45°. In addition, a small amount of synthesized BNNTs were also found to adhere inside the tube after the annealing process forming new layers which were unable to be retrieved. Therefore, the amount of produced nanotubes at the optimized annealing condition does not reflect the true efficiency as it is unknown how much quantity of powders are stuck on the tube surface and how much quantity of powders are really annealed.

A comparison of nanotube yield synthesized through recently developed various method is showed in Table 4.2. The highest amount of nanotube synthesized in the CVD method is reported as 200 mg by C. Zhi et al [189] while no quantification is available for the ball milling and annealing method. Using the rotating furnace in this research the maximum amount of BNNT was obtained 510 mg by blowing of powders. On the other hand, the
The highest amount of BNNT synthesized till date was obtained through Plasma method (35 g/h) as reported by Aidin Fathalizadeh et al. However, a high amount of gas flow rate was used in that method along with a special equipment. Therefore, considering the processing parameters it can be assumed that the nanotube yield could be much higher in the rotating furnace if the gas flow rate can be much higher when a greater amount of ball milled powder is inserted. Nevertheless, the quality and quantity of BNNTs obtained in this research are comparable with other synthesis techniques.

### 4.4 Conclusion

BNNTs were synthesized using ball milling and annealing method with a newly developed rotating furnace. The processing of ball milled powders in the rotating furnace was systematically studied for large quantity and high density of BNNTs for the use in composite materials. The synthesis conditions were optimized based on various annealing temperature, time and gas flow rate. Nanotube yield in the rotating furnace was higher than the conventional tube furnace as powders are continuously exposed to the gas by the rolling of powders during rotation of furnace. An annealing temperature of 1200 °C for 3 h was found to yield a large quantity of high density nanotubes. Nanotubes are entangled to each other and mostly formed large spherical particles due to rolling of powders. Nanotube yield was further improved when powders were inserted at high temperature i.e. 1200°C. Inclusion of steel balls with the powders helped rolling of powders efficiently resulting in highly dense but coarse nanotubes although the balls could not withstand at high temperatures. Such a very high density nanotube was obtained due to effective growing of nanotube at high temperature, rolling of powders by the balls and possible contributions of catalysts. The highest density and largest quantity nanotubes were obtained when the powders were annealed under suspension using N₂+5%H₂ gas at a flow rate of 4 l/min. It is expected that employing a nozzle at the tip of thin alumina tube might help in less consumption of gas for blowing of powders. The BNNTs synthesized with rotating furnace was used as reinforcement in Ti for preparation of titanium matrix composites.
5 Boron Nitride Particle Reinforced Titanium Matrix Composite

5.1 Introduction

Boron nitride (BN) is a ceramic material with a hexagonal and cubic crystal structure, which has high hardness, lightweight, good oxidation resistance and, most importantly, good thermal stability that made it suitable for high temperature applications. It is expected that introducing such light metal ceramic particles into the Ti metal matrix will deliver superior mechanical properties by dispersion hardening mechanism once a fully dense and pore free microstructure is obtained [221]. Boron nitride particle has an affinity to titanium for making bonds and reactions by forming TiN, TiB₂ and TiB compounds which are stable in high temperatures. These compounds exhibit high Young’s modulus of 550 GPa [50], high fracture toughness of 5 MPa.m^{1/2} [39] and greater corrosion, chemical and oxidation resistance [79]. The in situ formation of TiB, TiB₂ and TiN phases at the matrix-reinforcement interface or as a second phase may pose an added advantage by improving fatigue and wear properties of Ti matrix composites [36].

Cubic boron nitride (c-BN) particles have a high level of hardness making them suitable for preparation of hard materials such as cutting tools for machining of quenched steel and cast iron. These hard materials are formed using Ti powders acting as a binder [88-92]. On the other hand, hexagonal boron nitride (h-BN) particle has mostly been reinforced in Ti for the preparation of ceramic matrix composites with superior mechanical properties [36, 37] consisting of TiN and TiB₂ phases [38-42]. Furthermore, the reaction between Ti, B and N system is exothermic, which leads to the self-propagating high temperature synthesis (SHS)/combustion synthesis of the composite [80-82]. Preparation of SHS composite requires low temperature and is a simple process. It has been mentioned that SHS conditions may start at the concentration range from 5wt%BN to 15wt%BN and the yield product is equal for both TiN and TiB compounds [83].
In this research, h-BN particle reinforced titanium matrix composite (TMC) was fabricated by conventional pressing and sintering through the powder metallurgy route. The microstructural behaviour of the prepared composite was investigated and mechanical properties were optimized depending on processing parameters and fraction of reinforcements in the composite. The main objective was to understand the distinguishing effects between BN particles and nanotubes reinforcement on the microstructure and mechanical properties of the composites. The effect of nanotube reinforcement on the microstructural and mechanical properties of the composite has been discussed in chapter 6.

5.2 Experimental

Ti powders (<149 \mu m, 99.4\%, Johnson Matthey Catalog Company) and h-BN powders (<10 \mu m, U K Abrasives Inc) were mixed in proportion of 0~5vol\% reinforcement, considering titanium density as 4.506 g/cm\(^3\) and h-BN density as 2.34 g/cm\(^3\) [92]. The powder mixture was ultrasonicated for a short duration and gentle ball milling was performed in a high energy ball milling machine (Fig 3.3) at a speed of 100 rpm for 20 min in Ar atmosphere using 1 mm stainless steel balls with ball to powder weight ratio 2:1. Gentle ball milling effectively dispersed BN particles in Ti powders without damaging the structure of reinforcing particles. Composite powder of 1.2 g was loaded into a die (Fig 3.5) and pressed uniaxially at room temperature in a pressing machine (Fig 3.6) to fabricate 6 mm x 9 mm cylindrical green compacts. Sintering of the green compact was carried out at a temperature range from 800°C to 1200°C for 1~3 hrs in Ar atmosphere with a low heating rate of 5°C/min.

The density of the composite was measured by the Archimedes method and grain sizes were measured by the line intercept method [208]. For microstructural observation, the composites were cut into slices, mounted in polyfast, grounded in SiC emery papers and finally polished using OPS solution. The composite samples were etched using Kroll’s reagent (5 ml HF, 10 ml HNO\(_3\) and 85 ml H\(_2\)O) to observe the microstructural feature of phases. Olympus DP71 optical microscope was used to observe the cross-sectional microstructure and morphology of the grains in the composites. X-ray diffractometry (XRD) of the powders and sintered bulks were conducted in a PANalytical X’pert Pro MRD XL machine using C\(_{\alpha}\) radiation (0.154056 nm) in the 2\(\theta\) range of 10~110°. Powder morphology, distribution of powders and fracture surfaces of the composite were observed by scanning electron microscope (SEM) using a Zeiss Supra 55 VP FEG SEM.
For compression test, the sintered composites were machined in a turning machine into 4.67 mm (diameter) x 7 mm (length) cylinders with 1.5 aspect ratio (Fig 3.11). Compression testing of the composite was performed in an Instron 8801 machine (100 kN) at room temperature at a cross head speed of 0.005 mm/s. Hardness of the composites was evaluated using a Vickers micro hardness tester using a load of 98.07 N and dwell time of 10 s.

5.3 Results and Discussion

5.3.1 Powder Morphologies, Mixing and Phases

The morphology of the Ti powder used in this research as a raw material is shown in Fig 5.1a. The SEM image shows that the sponge powder particles are highly irregular in shape with a wide size distribution. Most of the particles are elongated in nature and bent in a crescent form. Some powders, in the form of an interconnected web could also be observed. These particles contain a large amount of porosity, which has a significant effect on the final product. The higher magnification image in Fig 5.1b reveals a clean

Figure 5.1: Starting (a, b) Ti powders and (c, d) h-BN powders; (a, c) low magnification and (b, d) high magnification
particle surface without any inclusions. The particle surfaces have a layered structure with ripples and a twisted shape on it. On the other hand, h-BN powders are flaky in shape (Fig 5.1c) representing a disc type morphology. Their smooth surface, lower density and large surface area caused them to become agglomerated (Fig 5.1d). The size differences between Ti and h-BN powders seems reasonable for homogeneous mixing, as much smaller h-BN particles may segregate in the mixing process. XRD pattern obtained from Ti powders as shown in Fig 5.2a exhibits the hcp crystal structure of the starting pure Ti powders. The sharp peaks from (100), (002) and (101) planes in the XRD pattern confirms the high crystallinity of these powders. In the case of h-BN powders, the main peak appears at around 26.75° that corresponds to (0002) plane for hexagonal crystal structure. The high intensity from this peak features the high crystallinity state of the h-BN powders.

The distribution of reinforcing h-BN powders in Ti powders after mixing was observed by SEM for various powder compositions and the images for Ti-5vol%BN mixture are shown in Fig 5.3 (a, b & c). Despite a large particle difference, h-BN powders were uniformly distributed within the Ti powders. Ultrasonication processing disintegrated the powder agglomeration of h-BN powders and distributed them within Ti powders. The ball milling process further rearranged the powders and a homogeneous mixture was obtained. A homogeneous distribution of reinforcement affects the density and mechanical properties of the composite; thereby, it is an important parameter for composite preparation. High magnification reveals different kinds of h-BN dispersion.

Figure 5.2: XRD pattern obtained from (a) Ti powders and (b) h-BN powders
depending on the shape and size of Ti powders. For block type Ti powders (Fig 5.3b), h-BN particles are adhered on their surfaces, whereas they tend to fill the interstitial spaces in the case of porous Ti powders (Fig 5.3c). In either case, it is clear that the structural integrity of h-BN powders was retained after the mixing process. The obtained XRD from the powder mixture in Fig 5.3d shows a strong peak from Ti but a weak peak from the h-BN powders. The peak of h-BN powders only appeared after 2vol%BN reinforcement and became clearly visible in 4vol%BN content. This is usual for smaller crystallites with lower volume fraction contents.
5.3.2 Composite Microstructures and Phases

The relative density of the composites as a function of BN reinforcement and sintering condition is shown in Fig 5.4. A high density in the range of 95-97% was obtained in the sintered composites. In general, density increases with increasing sintering temperature and periods but fluctuates with the content of the reinforcement. At higher sintering temperatures, diffusion of atoms and molecules is higher, which eventually eliminates the pores from the microstructure resulting in higher density. Density of the composite sintered at 800°C was lowered as the BN content became higher. This occurs because of the low density of the h-BN particles. However, density increases with the increasing content of BN reinforcement when composites were sintered at 1000°C and 1100°C. The increasing content of BN filling the gaps within Ti powders reduced the diffusion path and the longer sintering time provided more opportunity for the atoms and molecules to be diffused in the surroundings. At this higher sintering temperature, reaction between the matrix and reinforcement takes place resulting in in-situ formed second phase at the expense of reinforcements. Therefore, the volume fraction of the second phase is higher in the composites with a higher amount of reinforcement. This second phase possesses higher density than BN and reduces the pores by occupying void spaces in the microstructure and increasing the density. In contrast, composites sintered at 1200°C for

![Figure 5.4: Relative density of h-BN reinforced Ti composites](image-url)
3 h showed increased density up to 3vol%BN reinforcement and then decrease rapidly. This also might be due to second phase formation affecting the microstructure of the composite.

The phases of the composite were analysed from the XRD pattern, as shown in Fig 5.5. Here it is necessary to mention that XRD pattern, cross-sectional OM image and Vickers hardness testing was conducted only for the composites sintered at 800°C and 1000°C. Because of very high hardness of 1100°C and 1200°C sintered composites, they could not be cut using SiC blades in an Accutom machine. However, no other phases, except α-Ti, were observed in 800°C sintered composites. On the other hand, composites sintered at 1000°C showed TiB phase along with α-Ti phase. The TiB phase is only visible in the

Figure 5.5: XRD pattern obtained from composites sintered at (a) 800°C for 1 h (b) 1000°C for 1 h (c) 1000°C for 3 h and (d) enlarged view of Ti-5vol%BN composition for comparison; (i) pure Ti (ii) Ti-0.5vol%BN (iii) Ti-1vol%BN (iv) Ti-2vol%BN (v) Ti-3vol%BN (vi) Ti-4vol%BN (vii) Ti-5vol%BN
composites with a higher amount of BN reinforcement. No peak from h-BN phase was seen in the XRD patterns. A comparison of the XRD pattern for Ti-5vol%BN composition in Fig 5.5d shows stronger TiB peaks with higher sintering temperature and period. This indicates that the reinforcing h-BN agent tend to react with Ti at higher sintering temperatures, transforming them to the TiB phase. As the sintering temperature increases, the amount of BN in the matrix decreases but the volume fraction of TiB increases at the expense of BN reinforcement. This suggests that composites sintered at 1100°C and 1200°C consequently will possess larger amount of TiB phase but a smaller amount of BN particles.

The effect of sintering conditions on the grain size and its morphology of the composites was analysed by optical microscopy. The cross-sectional microstructure of the composites with 0, 1, 3 and 5vol%BN reinforcement sintered at 800°C for 1 h, 1000°C for 1 h and 1000°C for 3 h, is illustrated in Fig 5.6, 5.7 and 5.8, respectively. Unreinforced pure Ti has coarse grain size and with the addition of reinforcements the grain sizes are reduced but contained higher amount of pores. The grains also tend to be equiaxed as the reinforcement and sintering temperature increased especially at a temperature above 800°C. The grains of 800°C sintered composites are non-uniform and slightly elongated in shape. The presence of a prior particle boundary is clearly evident in the microstructure. This inhomogeneous microstructure evolved as a result of lower diffusion of atoms and molecules caused by lower sintering temperature and periods. On the contrary, grain sizes become uniform and semi-equiaxed morphology when composites are sintered at 1000°C.

During consolidation of powders, powder particles come into intimate contact and larger pores collapse. In the green compact, particles that are in contact form a neck like structure within the pores. In sintering, interparticle diffusion increases the necking and reduces the pore volume simultaneously followed by spherodization of pores and their elimination. That’s why the particle boundaries disappeared in the composites sintered at higher temperature. The remaining porosity observed in the microstructure is mainly from the highly irregular Ti particles. The measurement of grain sizes, as shown Fig 5.9, clearly exhibits the reduction of grain sizes in the composites by the reinforcements. Irrespective of sintering condition, the grain size of pure Ti is in the range of 30~33 μm, which is drastically reduced to 17~19 μm by 5vol%BN reinforcement. The presence of BN particles and in-situ-formed TiB in the matrix inhibited the grain growth during the sintering process resulting in fine grains. Sintering temperature and periods showed little
Figure 5.6: Cross-sectional microstructure of the composite sintered at 800°C for 1 h (a) pure Ti (b) Ti-1vol%BN (c) Ti-3vol%BN (d) Ti-5vol%BN

Figure 5.7: Cross-sectional microstructure of the composite sintered at 1000°C for 1 h (a) pure Ti (b) Ti-1vol%BN (c) Ti-3vol%BN (d) Ti-5vol%BN
Figure 5.8: Cross-sectional microstructure of the composite sintered at 1000°C for 3 h (a) pure Ti (b) Ti-1vol%BN (c) Ti-3vol%BN (d) Ti-5vol%BN

Figure 5.9: Average grain size of composites as a function of BN reinforcement and sintering conditions
effect on the grain size but they homogenized the grains which gave them an almost equiaxed morphology. The distribution of TiB phase in the matrix was observed by SEM from the cross-sectional microstructure of the composites after etching. Fig 5.10a and 5.10b shows the images of Ti-0.5vol%BN and Ti-5vol%BN composites sintered at 1000°C for 3 h, respectively. Fine long needles, along with a few coarse TiB whiskers,

Figure 5.10: Distribution of TiB phase in (a) Ti-0.5vol%BN and (b) Ti-5vol%BN composites sintered at 1000°C for 3 h; (c) thin long TiB needles with high aspect ratio (d) Short and thick TiB plates (e) slab like TiB plates (f) cluster of TiB needles
are embedded in the composite matrix with a lower content of BN. TiB whiskers are randomly oriented without any fixed pattern, growing along [010] direction [64]. A higher concentration of TiB whiskers having a coarser structure was observed in 5 vol% reinforced composite. The coarse TiB whiskers are mostly located in the areas of clusters. Dimples around these TiB phase are noticeable, which is due to erosion of the Ti matrix during polishing. This implies that TiB is a hard material but their interface with the Ti matrix is not strong enough to sustain the load transfer from matrix to TiB. Mainly two kinds of TiB morphology; thin and long needle type TiB with high aspect ratio along with coarse and thick plate type whisker, was observed in the composite. Fig 5.10c shows a high aspect ratio TiB needle having ~6 μm length and ~300 nm diameter. They have lamellar structures along the longitudinal axis (i.e. needle axis), which is due to stacking disorder [4]. On the other hand, a short and thick TiB whisker has a thickness around 1 μm, as shown in Fig 5.10d. Their cross-section varied from hexagonal to polygon with the number of steps. Slab-like much coarser TiB plates (Fig 5.10e) and clustering of fine needles (Fig 5.10f) could also be observed in a few regions of the composite.

5.3.3 Mechanical Properties of Composites

The hardness of the composites sintered at different conditions was evaluated using micro-hardness tester and the average value of Vickers hardness is shown in Fig 5.11. As can be seen, hardness for pure Ti bulks is almost the same, irrespective of sintering conditions. However, hardness of the composite increased proportionally with the increasing amount of h-BN reinforcement. A big differences in hardness between 800°C and 1000°C sintered composites could also be observed. This difference in hardness is mainly due to increased density obtained in the composite along with formation of TiB phase in the matrix at 1000°C. The hardness observed in 800°C sintered composites is mainly due to the h-BN particles uniformly distributed in the matrix. On the other hand, most of the h-BN that reacted at 1000°C sintering temperature forming TiB phase, as identified in the XRD graph, was responsible for the increased hardness in these composites.
The representative stress-strain curve obtained from the compression test for h-BN reinforced Ti matrix composite performed at room temperature is shown in Fig 5.12. With increasing amount of reinforcement, the strength of the composite increases but ductility decreases. The strength of the composite also increases with higher sintering temperature and longer periods. The effect of varying amount of reinforcement and sintering conditions on the mechanical properties of the composite is clear in Fig 5.13a and Fig 5.13b, where average compressive strength and reduction of length data calculated from the number of samples has been plotted, respectively. Unreinforced pure Ti sintered at 800°C for 1 h has a compressive strength of 686 MPa and the length is reduced up to 59%. This strength increases proportionally with the amount of h-BN reinforcement reaching a maximum strength of 1013 MPa with 16% length reduction by 5vol%BN reinforcement. This improved strength is mainly contributed by the h-BN particles, as they did not react with Ti under this sintering condition.

In other sintering conditions, i.e. when composites were sintered at 1000, 1100 and 1200°C, the highest compressive strength was obtained in the composites with 3vol%BN reinforcement. Pure Ti sintered at 1000°C for 1 h, 1000°C for 3 h, 1100°C for 3 h and
1200°C for 3 h, exhibited compressive strength of 690 MPa, 734 MPa, 681 MPa and 946 MPa, respectively. This strength was greatly increased to a maximum of 1322 MPa, 1284 MPa, 1362 MPa and 1470 MPa and experienced a reduction in length up to 15%, 12%, 15%, and 15% with only 3vol%BN reinforcement, respectively. The strength enhancement in these composites is contributed by the combinations of h-BN particles and in-situ formed TiB phases. However, their individual contribution is still unknown, as the exact proportion of TiB phase in the matrix could not be measured quantitatively. However, the qualitative analysis from XRD and fracture data suggests that above 800°C sintering temperature, the reinforcing h-BN particles starts to transform into TiB phase and the transformation is accelerated as the sintering temperature was increased. This means that composites sintered at 1000°C for 1 h are dominated by h-BN particles, compared with the composites sintered at 1000°C for 3 h. On the other hand, no h-BN particles survived when composites were sintered at 1100°C and 1200°C, leaving TiB phase only in the matrix. Moreover, apart from sintering temperatures, the volume fraction of TiB phase is also higher in the composite, which has a higher amount of h-BN reinforcement since BN acts as the source element for the transformed TiB phase. The matrix of these composites also possess large amount of N solid solution in Ti. Formation of greater amount of TiB in the 5vol%BN composite sintered at higher temperature accompanies residual stress at Ti-TiB interface. This residual stress together with already acting compressive stress originating from N solid solution leads to early failure of the composite before reaching their maximum value resulting in lower strength in the composites. The crack propagation in these composite is also faster limiting their plastic deformation relative to the 3vol%BN reinforced composites.

The presence of h-BN and TiB whiskers in the composite strengthens the composite by the dispersion hardening mechanism. The reinforced h-BN particles are mostly located at the grain boundaries, whereas TiB exist within the grains and grain boundaries. During deformation, dislocations within the grain multiply, increasing the dislocation density. As the deformation is in progress, these dislocations tend to move and encounter reinforcing BN particles and TiB whiskers. They cause obstacles in the movement of dislocation, resulting in dislocation bow out and Orowan looping followed by entanglements of dislocations [222]. In addition to dispersion hardening, solid solution strengthening of the composites also takes place within the composite and the effect is especially high in the composites sintered at higher temperatures. At higher sintering temperatures BN dissolves to B and N atoms. The light N atom easily diffuses to the Ti matrix, occupies
Figure 5.12: Representative stress-strain curve obtained from room temperature compression test of the composites sintered at (a) 800°C for 1 h (b) 1000°C for 1 h (c) 1000°C for 3 h (d) 1100°C for 3 h and (e) 1200°C for 3 h
interstitial sites of the matrix and the left over B atom reacts with Ti to form TiB whiskers, as long as 18.29wt% B is available [55]. In addition, Ti powder contains a small proportion of O, N, C, Fe and Cl as impurities. The impurities O, N and C form interstitial solid solution whereas Fe atoms substitutes Ti atom in the matrix. Their presence in the matrix generates stress field in the lattice and act as a pinning effect in restricting the movement of dislocations. The reduced grain size by BN reinforcement might also have slight effect on the strength of the composite by means of the Hall-Petch relationship [223]. According to this relationship, the yield strength is inversely proportional to the grain size. Smaller grain sizes in composites mean a larger grain boundary area and this larger grain boundary area is more effective in making barrier for dislocation gliding and movement thus increasing the strength of the composite.

Figure 5.13: (a) Maximum compressive strength and (b) reduction of length of the composites with respect to sintering conditions and reinforcement content
5.3.4 Evaluation of Composite Fracture Surfaces

The fracture surfaces of the composite samples after compression testing were observed by SEM in order to analyse the distribution of reinforcing BN particles and TiB reaction phases in the matrix and their effect on the mechanical properties of the composite. Fig 5.14 represents the fracture surface from the Ti-5vol%BN composite sintered at 800°C for 1 h. A low magnification image (Fig 5.14a) of the fracture surface shows mainly

Figure 5.14: Fracture surfaces of Ti-5vol%BN composite sintered at 800°C for 1 h; (a) low magnification image of fracture surface (b) high magnification image showing ductile type fracture (c) distribution of h-BN particles in the matrix (d) structural integrity of h-BN particles (e) cluster of h-BN particles (f) reaction at Ti-BN interface
ductile type fracture occurred in the composite during its deformation. The presence of elongated shear bands and dimples (Fig 5.14b) is visible where particle debonding occurred as a result of applied force. The flake-shape BN particles were also seen in many places and they are uniformly distributed in the composites (Fig 5.14c). Closer observation reveals that the reinforcing BN particles are still intact without any structural damage (Fig 5.14d). This indicates that BN particles are able to withstand high pressure and temperature applied during the preparation of these composites. The good distribution

Figure 5.15: Fracture surfaces from Ti-3vol%BN composite sintered at 1000°C for 1 h; (a) low magnification and (b) high magnification image of fracture surface (c) retained h-BN particles (d) BN particles pull out from matrix (e) randomly oriented TiB whiskers (f) pull out of TiB whiskers from the matrix during deformation
and structural integrity of BN particles in the composite effectively transferred the load from the Ti matrix to the reinforcing BN particles. This is justified by the proportional increase of Vickers hardness and compressive strength, even up to 5 vol% BN reinforcement in the composite, as seen in Fig 5.11 and 5.13a. A small number of BN clusters (Fig 5.14e) and a very low fraction of TiB reaction phases (Fig 5.14f) were also observed in some regions of the composite.

The fracture surface of Ti-3vol%BN composites sintered at 1000°C for 1 h corresponding to the maximum compressive strength is shown in Fig 5.15. The sharp edges and abrupt changes on the surface indicate that the fracture occurred in a brittle manner (Fig 5.15a). Higher magnification (Fig 5.15b) shows cleavage of particles took place within the composite while it was under load. The reinforcing BN particles were seen in many places, which are either fractured or partially reacted with Ti matrix (Fig 5.15c). The pull out of BN particles from the matrix indicates that the load was effectively transferred from Ti matrix to the BN particles (Fig 5.15d). A good proportion of TiB whiskers randomly oriented in Ti matrix were also observed in the fracture surface (Fig 5.15e).

Figure 5.16: Fracture surfaces from Ti-3vol%BN composite sintered at 1000°C for 3 h; (a) low and (b) high magnification image (c) occurrence of ductile fracture in the region where h-BN particles and TiB whiskers are absent (d) in-situ formed TiB whiskers
Most of these did not experience any fracture, rather they pulled out from the matrix during loading and deformations (Fig 5.15f). This indicates high hardness of TiB phases, which contributed strength to these composites together with BN particles. A longer sintering time (up to 3 h for this composite) results in more brittle fracture, as can be seen in Fig 5.16 (a & b). Nevertheless, ductile modes of fracture (Fig 5.16c) were observed in very few places where no BN reinforcement particles or TiB reaction phases exist. No BN particles could be observed in the matrix implying that they all have taken part in the reaction and transformed to TiB phases leaving only TiB whiskers in the composite (Fig 5.16d). The excess amount of TiB formed in this composite rendered slightly increased hardness and compressive strength, as can be seen from Fig 5.11 and Fig 5.13, respectively. The fracture surface analysis of the composites sintered at 1100°C and 1200°C exhibited a similar kind of pattern consisting of TiB whiskers in Ti matrix and experienced a cleavage type failure.

Hexagonal boron nitride particles are much harder relative to pure Ti particles. During sintering, reaction between Ti and BN particles takes place that initially forms titanium boride phase at the interface. This reaction phase gradually grows as the sintering is in progress. The formation of reaction phase at the interface makes a good bonding between BN particles with Ti matrix. However, there is an optimum thickness of reaction phase that gives the maximum strength. The cleavage of BN particles under deformation as shown in Fig 5.14 and 5.15 after sintering at lower temperatures (e.g. 800°C/1000°C for 1 h) indicates that the thin interfacial reaction phase is much stronger and transferred the load from Ti matrix to BN particles through the reaction phase. Thus it strengthens the composite. A higher sintering temperature and longer sintering time (e.g. 1000°C/1100°C/1200°C for 3 h) dissolves more BN particles resulting in completely new TiB phase (Fig 5.16) which acts as in-situ reinforcement in the composites. It is noticeable that the maximum Vickers hardness for 1000°C sintered composites (Fig 5.11) was obtained in Ti-5vol%BN composite but maximum compressive strength was obtained in Ti-3vol%BN composite (Fig 5.13). This phenomenon is associated with the behaviour of the deformation process during Vickers hardness and compression testing. Vickers hardness only measure local strength of the composite depending on the size and shape of indentation. On the other hand, failure of the composite during the compression test initiates from the pores present in the matrix. It is well known that the formation or presence of pores acts as stress concentrator. During compression test the shearing between matrix and reinforcement occurs. This causes to increase the fraction of pores in
the composites which is already present in the microstructure and leads to the failure. Besides, excess TiB phases imparting excessive hardness and high residual stress limits the deformation process and leads to the catastrophic failure of the composite.

5.4 Conclusion

BN particle reinforced Ti matrix composite was successfully manufactured in this research through the powder metallurgy route. The gentle ball milling operation was able to distribute BN particles uniformly within Ti particles. A high density, in the range of 95–97%, was obtained in the sintered composites and this density increased with increasing sintering temperature. The composite also contained higher numbers of pores with the increasing amount of reinforcements. XRD pattern obtained from the composite showed the formation of a TiB phase in the composite by the reaction between Ti and BN particles. This TiB formation is higher in the composites which are sintered at higher temperatures and for longer periods. Cross-sectional microstructure showed that grain refinement took place in the composite as a result of BN reinforcement and the formation of TiB phases.

Observation of the fracture surface from 800°C sintered composite demonstrates that BN particles are uniformly distributed in the matrix along with slight formation of TiB phases in several places and experience ductile type failure during compression test. On the other hand, the reactions between Ti and BN progress as the sintering temperature goes up to 1000°C for 1 h. At this sintering condition, the TiB phase dominates in the matrix and plays a major role in strengthening the composites leading to brittle type fracture. In contrast, no evidence of BN particles could be observed when these composites were sintered for up to 3 h. indicating their complete transformation to TiB phases.

The hardness of the composite increased proportionally with the increasing amount of reinforcements, sintering temperature and time. The hardness of the Ti-5vol%BN composite sintered at 800°C for 1 h was 291 HV, which increased to 390 HV when composites were sintered at 1000°C for 1 h. Composites sintered at 800°C for 1 h showed maximum compressive strength of 1013 MPa for Ti-5vol%BN composition. This strength is provided solely by the BN particle reinforcements. In contrast, Ti-3vol%BN composition exhibited maximum compressive strength when composites were sintered at 1000°C, 1100°C and 1200°C where TiB phases dominate. The highest compressive
strength of 1470 MPa was obtained in these kinds of composites when sintered at 1200°C for 3 h.

The microstructural behaviour and mechanical properties of h-BN reinforced Ti matrix composite would help to distinguish the effect of BN particle and BNNT reinforcement in the composites.
6 Boron Nitride Nanotube Reinforced Titanium Matrix Composite

6.1 Introduction

The attractive physical and mechanical characteristics of BNNTs recently triggered numerous researches on BNNT reinforced polymer [22-28] and glass [29, 30] matrix composites. Despite having all these special features, boron nitride nanotube reinforcement in metal matrix composite is still in early stage. Only a few numbers of investigations have been conducted recently for aluminium matrix composites [31-35] while no research has been conducted on titanium till to date. Incorporation of BNNTs in these aluminium matrix greatly improved the mechanical properties. The interfacial reaction zone is also thinner and much stable than other kinds of matrix-reinforcement interface [63]. Therefore, it can be assumed that BNNT could also be a potential reinforcement for titanium matrix composite.

For employing BNNT as reinforcement in metal matrix composites, a new production technique is necessary for obtaining large quantity and high density nanotubes. This was achieved by introducing new kind of rotating furnace and optimizing the synthesis conditions as shown in chapter 4. In this research, these BNNTs were reinforced in Ti matrix composite by the conventional cold pressing and sintering method [7] through the powder metallurgy route. The effect of processing conditions and nanotube reinforcement on the microstructure and mechanical properties of the composite was also analysed.

6.2 Experimental

The reinforcing boron nitride nanotubes were synthesized by ball milling and annealing method in the specially designed rotating furnace (Fig 3.9) using ball milled boron powders [197]. The detailed synthesis procedure has already been mentioned in the experimental section of chapter 4. The synthesized BNNTs were further processed by ultrasonification in acetone for purification. During ultrasonification, the nanotube containing top liquid was separated in 20 min intervals, allowed to deposit at the bottom and kept in an oven under vacuum to get rid of the acetone. Then the required amount of
Ti powders and synthesized BNNTs were mixed in proportion of 0~5vol% reinforcement considering titanium density as 4.506 g/cm³ and BNNT density as 2.25 g/cm³ [154]. The powder mixture was ultrasonicated for short duration and a gentle ball milling was performed in a high energy ball milling machine (Fig 3.3) at a speed of 100 rpm for 20 min in Ar atmosphere using 1 mm stainless steel balls with ball to powder weight ratio 2:1. Composite powders of 1.2 g were loaded into a die and pressed uniaxially at room temperature in a pressing machine (Fig 3.6) to fabricate 6 mm x 9 mm cylindrical green compacts. Sintering of the green compact was carried out in the temperature range from 800°C to 1200°C for 1~3 hrs in Ar atmosphere with a low heating rate of 5°C/min.

The density of the composite was measured by Archimedes method and relative density was calculated using theoretical density. The prepared composites were cut, mounted, grounded and polished for optical and scanning electron microscopy characterization. Samples were etched by Kroll’s reagent to observe grain morphology and phase distributions. The grain sizes of the composite was measured by line intercept method [208]. The phase analysis of the composite was performed by X-ray diffractometry. The morphology of the as synthesized BNNTs and fracture surface of the composite was observed by scanning electron microscope (SEM) using a Zeiss Supra 55 VP FEG SEM. Transmission electron microscopy (TEM) of nanotubes were conducted in a JEOL 2100 LaB6 machines. A JEOL 2100 FEG TEM was used to obtain high resolution electron image, diffraction pattern and energy dispersive x-ray spectroscopy (EDX) from the composite foil samples. For compression test, the sintered composites were machined in a turning machine into 4.67 mm (diameter) x 7 mm (length) cylinders with 1.5 aspect ratio. Compression test of the composite was performed in an Instron 8801 machine (100 kN) at room temperature and 500°C at a cross head speed of 0.005 mm/s.

6.3 Results and Discussion

6.3.1 Boron Nitride Nanotubes

Boron nitride nanotubes synthesized by the ball milling and annealing method in the specially designed rotating furnace are shown in Fig 6.1. A high density of nanotubes clustered and entangled with each other could be seen in the SEM image of Fig 6.1a. The synthesized nanotubes were a few microns in length with diameters ranging from 30 nm to 100 nm (Fig 6.1b). A high magnification TEM image of the synthesized nanotubes
shows bamboo like structures featuring knots and joints stacked on each other (Fig 6.2a). In the synthesis, the majority of nanotubes were grown in the form of the bamboo structure while a few cylindrical structured nanotubes having internal plain edges were also synthesized (Fig 6.2b). Metal catalyst particles that help grow the nanotubes are located at the tip of nanotubes. These catalyst particles, mainly consisting of Fe, Ni and Cr, originate from the ferric nitrate catalyst, milling balls and container. The nanotubes were also accompanied by a small amount of nanoparticles found during the synthesis process. In the annealing process all of the ball milled boron particles could not come into contact with the reaction gas. Hence, these nanoparticles are retained within the powder.

Figure 6.1: SEM image of as synthesized boron nitride nanotubes;
(a) low magnification (b) high magnification

Figure 6.2: TEM image of (a) bamboo structured and (b) cylindrical structured boron nitride nanotubes
samples without growing. This is usual in nature as full conversion of particles to nanotubes is extremely difficult. The XRD pattern obtained from the synthesized boron nitride nanotube (Fig 6.3) showed a hexagonal crystal structure. The appearance of (0002) basal plane at 26.68° represents the main peak for the hexagonal boron nitride phase. Peaks from Fe contamination also appear at 35.66° and 44.7° originating from the catalyst.

![XRD pattern from synthesized boron nitride nanotubes](image)

Figure 6.3: XRD pattern from synthesized boron nitride nanotubes

### 6.3.2 Purification of the Nanotubes

Boron nitride nanotubes synthesized in the rotating furnace were grown on the surface of large particles (Fig 6.4). The morphology of these particles are either spherical, semi-spherical or lumped in nature. These large particles mainly consist of entangled as-grown nanotubes on the surface with agglomerated sintered nanoparticles inside the core. Initially, the rotation of furnace causes aggregation of the ball milled nanoparticles. As the annealing proceeds, the outer ball milled particles start to grow into nanotubes as a result of the nitriding reaction while inside the particles become sintered. It appears that with continued furnace rotation, the surrounding as-grown nanotubes comes into contact with the agglomerates, entangles and enlarge their sizes.
For effective nanotube reinforcement in the composite it is important to remove all of these large particles from the synthesized nanotubes. Therefore, ultrasonification of the as-synthesized nanotubes was performed in acetone for two hours and the top liquid was separated in twenty minutes intervals so that excessive sonication did not damage the nanotube structure or shorten it. Another advantage of ultrasonification is that it disentangles the clustering of nanotubes. Without ultrasonification it was impossible to stop the nanotube agglomeration even after the ball milling. Excessive ball milling is responsible for damage or shortening of nanotubes. A gentle ball milling may disperse the nanotubes but the large particles still occupy the void spaces between Ti particles as can be seen from Fig 6.5. These particles will have a detrimental effect on the mechanical properties of the composite. This indicates that purification of nanotube by ultrasonification is a necessary precondition for preparation of composites. Fig 6.6 shows
the morphology of the extracted boron nitride nanotubes from the ultrasonicated liquids at different intervals of ultrasonification period. During ultrasonification the lower density nanotubes break up from the agglomerated large particles and then float to the top of the solution while the heavier agglomerated and sintered particles remain deposited at

Figure 6.6: Boron nitride nanotubes extracted after ultrasonication at (a) 30 min (b) 60 min (c) 90 min and (d) 120 min

Figure 6.7: Residual particles after 120 min ultrasonication; (a) low magnification and (b) high magnification
the bottom. Fig 6.7 shows the image of residual large particles after ultrasonification for 120 minutes. As can be seen from the micrograph almost all of the nanotubes were able to break up from the large particles leaving the particles only at the bottom.

6.3.3 Composite Powder Mixtures

The mixture of Ti particles and BNNTs obtained after ultrasonification and ball milling are shown in Fig 6.8. Nanotubes dispersed on the surfaces of Ti particles (Fig 6.8a) are still a few microns in length after ultrasonication and ball milling. This means, the milling was able to distribute the nanotubes without shortening or structural damage (Fig 6.8b).

Cluster of nanotubes are also seen in many places where they act as filler material between the gaps of larger Ti particles (Fig 6.8c). Ti particles used in this research were sponge type and highly irregular in shape, having porous structures. During the mixing process, BNNTs easily occupy the interstitial places. This is unavoidable and common in all kinds of bimodal powders with big differences in particle sizes [105]. Nevertheless, the mixing
of Ti particles and BNNTs was remarkable as homogeneous mixing was obtained in respect to the distribution of either individual nanotubes or their clusters (Fig 6.8d). The XRD pattern obtained from this powder mixture, as shown in Fig 6.9, exhibited only hcp Ti phase with the main peak at 40.1° corresponding to the (101) plane. No evidence of boron nitride could be found in the XRD pattern. The diameter of nanotubes are in the nanoscale range and compounds with low volume fraction are harder to detect in XRD. According to Scherrer equation [224] the crystallite size is inversely proportional to the peak width

\[ B(2\theta) = \frac{K\lambda}{L\cos\theta} \]

Where \( B \) is the full width at half maximum (FWHM), \( L \) is crystallite size, \( K \) is Scherrer constant, \( \lambda \) is wavelength and \( \theta \) is the Bragg angle. As the crystallite size becomes smaller the width of the peak becomes wider. Accordingly the nanotubes in the powder mixture supposed to result in wide peaks and its intensity compared to Ti particles would be harder to detect from the XRD pattern.

Figure 6.9: XRD pattern obtained from the mixture of Ti and BNNTs; (a) Pure Ti (b) Ti-0.5vol%BNNT (c) Ti-1vol% BNNT (d) Ti-2vol%BNNT (e) Ti-3vol%BNNT (f) Ti-4vol%BNNT and (g) Ti-5vol%BNNT
6.3.4 Microstructure and Phases of Composites

Fig 6.10 shows the relative density of the sintered composites as a function of different sintering conditions and BNNT reinforcement. A high density in the range of 95-97% was obtained in the sintered bulks. In general, the density of the composite increased with increasing sintering temperature and time. Temperature is the driving force for diffusion of atoms and molecules. At higher sintering temperature and longer sintering period, the rate or volume of diffusion is higher and this substantially reduced the pores in the matrix. However, the density remained almost constant, with only a slight drop, as the content of BNNT reinforcement increased in the composite. The lower density of the nanotubes, fraction of second phases formed in the composite and greater amount of pores might be responsible for the drop of density at higher reinforcement. The potential for formation of second phases by the reaction of Ti matrix and BNNTs were studied using the XRD data. Apparently no other phases except $\alpha$-Ti could be observed in the XRD patterns obtained from the sintered composites as shown in Fig 6.11. The intensity of the reaction phases was comparatively much lower than the intensity of $\alpha$-Ti. Besides, a faster scanning produced noise in the pattern that making difficult to distinguish low intensity peaks. As a result, a slower scan for Ti-5vol%BNNT composites sintered at various

![Figure 6.10: Relative density of titanium matrix composites with BNNT content](image)

111
conditions were carried out and the comparison of peaks are illustrated in Fig 6.12. The analysis indicates the formation of TiB phase in the composite by the reaction between Ti and BNNTs. According to Ti and B binary phase diagram [55], B atom spontaneously reacts with Ti at high temperature to form TiB compound as long as B concentration is available up to 18.29 wt%. At lower sintering temperature, a weak peak appears at an angle of 42.2° corresponding to (102) plane of orthorhombic TiB phase in the XRD pattern. However, as the sintering temperature increases from 800°C to 1200°C, the intensity of the TiB phase becomes stronger. It implies that the reaction accelerates further at an elevated sintering temperature.

Figure 6.11: XRD pattern obtained from the composite sintered at (a) 800°C for 1 h (b) 1100°C for 3 h (c) 1200°C for 3 h and (d) 1200°C for 3 h; (i) pure Ti (ii) Ti-0.5vol%BNNT (iii) Ti-1vol%BNNT (iv) Ti-2vol%BNNT (v) Ti-3vol%BNNT (vi) Ti-4vol%BNNT (vii) Ti-5vol%BNNT
The cross-sectional microstructure of the titanium matrix composites after etching was examined by optical microscopy in order to understand the effect of various sintering conditions on the morphology and distribution of reaction phases and grain sizes. The OM images of the composites sintered at various sintering conditions are shown from Fig 6.13 to Fig 6.16 for 0, 1, 3, and 5 vol% BNNT reinforcement. As can be seen most of the grains have an equiaxed morphology along with few elongated grains regardless of the BNNT content and sintering conditions. The grain morphology becomes uniform and more equiaxed in shape as the amount of BNNTs reinforcement and sintering temperature increased. It seems sintered pure Ti bulks possess a larger grain size and the grains become refined but contains higher amount of pores with the addition of reinforcements. The high porosity with the increasing BNNT reinforcement most probably occurs due to greater resistance to deformation by the nanotubes during pressing compared to ductile nature of pure Ti. The grains of 800°C sintered composites are non-uniform and slightly elongated in shape. The presence of the prior particle boundary is also clearly visible in the microstructure. This inhomogeneous microstructure evolved because of lack of diffusion of atoms caused by lower sintering temperature and periods. During consolidation of powders, powder particles come through intimate contact and larger
Figure 6.13: Cross-sectional microstructure of composite sintered at 800°C for 1 h; (a) pure Ti (b) Ti-1vol%BNNT (c) Ti-3vol%BNNT (d) Ti-5vol%BNNT

Figure 6.14: Cross-sectional microstructure of composite sintered at 1000°C for 3 h; (a) pure Ti (b) Ti-1vol%BNNT (c) Ti-3vol%BNNT (d) Ti-5vol%BNNT
Figure 6.15: Cross-sectional microstructure of composite sintered at 1100°C for 3 h; (a) pure Ti (b) Ti-1vol%BNNT (c) Ti-3vol%BNNT (d) Ti-5vol%BNNT

Figure 6.16: Cross-sectional microstructure of composite sintered at 1200°C for 3 h; (a) pure Ti (b) Ti-1vol%BNNT (c) Ti-3vol%BNNT (d) Ti-5vol%BNNT
pores are collapsed. In the green compact, particles which are in contact form a neck like structure within the pores. During sintering, interparticle diffusion grows the neck and reduces the pore volume simultaneously followed by spherodization of pores and its elimination. That’s why the particle boundaries disappeared in the composites sintered at higher temperatures. The average grain sizes of the composite with respect to BNNT content and sintering condition is plotted in Fig 6.17. The grain size of the composite decreases as the reinforcement content increases. Pure Ti sintered at 800°C, 1000°C and 1100°C has a grain size around 30 μm which is reduced to 25 μm, 20 μm and 18 μm, respectively, when 5vol%BNNT was reinforced. The pinning effect of dispersed BNNTs and in-situ formed TiB second phase in the matrix inhibited the grain growth during sintering period. The unreinforced pure Ti sintered at 1200°C for 3 h showed much larger grains of 51 μm though it is also reduced to 25 μm with 5vol%BNNT reinforcements. The higher diffusion rate of molecules at this elevated temperature superseded the pinning effect that turns the grain larger. In high temperature especially above the beta transus temperature, the self diffusion of Ti atom is a few orders of magnitude higher than the room temperature [43]. This causes rapid diffusion of Ti atoms in the matrix resulting in

![Figure 6.17: Average grain size with BNNT reinforcement and sintering conditions](image)

...
The elimination of pores followed by grain growth. The effect of sintering temperature on the formation of the second phase is also evident by the presence of TiB whisker in the composite microstructure sintered at 1000, 1100 and 1200°C. No TiB phase could be observed in the composite sintered at 800°C for 1 h. Two distinct morphology of TiB phase: needles with high aspect ratio and plate like coarse whisker were formed in the matrix as shown in Fig 6.18a and Fig 6.18b, respectively. According to Hall-Petch relationship [223], the yield strength of a polycrystalline material increases with decreasing grain size.

\[
\sigma = \sigma_0 + K \cdot d^{-0.5}
\]

Where, \(\sigma\) is the yield strength, \(\sigma_0\) is the material constant for dislocation movement, \(K\) is the strengthening coefficient dependent on material and \(d\) is the grain size. When a stress is applied on the material, it causes the generation of dislocations within the grains. As the stress continues, the dislocation density increases and there are dislocation pile ups. In Ti-BNNT composites, the dispersion of BNNTs and in-situ formed TiB second phase reduced the grain size. This reduction of grain size contributes in strengthening the composite by means of grain boundary strengthening.

### 6.3.5 Room Temperature Mechanical Properties

The mechanical properties of the composite was evaluated by conducting compression tests on the cylindrical samples. Fig 6.19 shows the room temperature stress-strain plot for the composites in respect of BNNT reinforcement and sintering conditions. The
strength of the composite increases with an increasing amount of reinforcement and sintering temperatures at the expense of ductility. The strength-ductility relationship of the composites is conspicuous in Fig 6.20. The highest room temperature compressive strength was obtained with 4vol%BNNT reinforced composites irrespective of sintering conditions. The compressive strength of pure Ti bulks sintered at 800°C for 1 h was 678 MPa. As the reinforcement increased to 4vol%BNNT, the compressive strength increased.

Figure 6.19: Stress-strain curve from the room temperature compression test of composites sintered at (a) 800°C for 1 h (b) 1000°C for 3 h (c) 1100°C for 3 h and (d) 1200°C for 3 h
to 984 MPa. An increase in strength by 45% from only 4vol%BNNT reinforcement is a significant enhancement in the mechanical properties of the composite. This increment of strength is mainly contributed by the nanotube reinforcement. Similar strength increment pattern and drop of ductility were also observed when the composites were sintered at higher temperatures and longer periods of time. For example, Ti-4vol%BNNT composite sintered at 1000°C for 3 h, 1100°C for 3 h and 1200°C for 3 h have compressive strengths of 1330 MPa, 1421 MPa and 1396 MPa, respectively. Relative to the sintering condition of 800°C for 1 h with the same composition, the strength rose by 35%, 44% and 42%, respectively. This increase in strength comes from a combined effect of grain size, boron nitride nanotube reinforcement, in-situ formed TiB phase and solid solutions.

It is evident that there is a big differences in strength between the composites sintered at 800°C and above this temperature. The strengthening of composites sintered at 800°C is primarily contributed solely by the boron nitride nanotubes reinforcement. At this temperature the BNNTs start to react with Ti and forms a layer of reaction phase at the Ti-BNNT interface. When the sintering temperature goes above 800°C, the reaction proceeds in a severe manner. With the elapse of sintering time, BNNTs starts to dissolve into B and N atoms. The N atom diffuses to the Ti matrix and occupies interstitial sites to form solid solutions. On the contrary, the left over B atom reacts to Ti atom forming in-situ TiB phase. The process is a function of temperature and time. Therefore, composites sintered at 1000°C, 1100°C and 1200°C is mainly dominated by the in-situ formed TiB phase rather than boron nitride nanotubes. The higher amount of BNNTs and in-situ
formed TiB phase present in Ti-5vol%BNNT composite acted as stress concentrators. This resisted plastic deformation under loading resulting in less strength and catastrophic brittle failure of the composite. The reduction of length at fracture as shown in Fig 6.20b represents an inverse behaviour of strength data. Pure Ti sintered at 800°C, 1000°C, 1100°C and 1200°C goes under deformation up to 58%, 48%, 49% and 36%, but this drops to 19%, 12%, 13% and 10% when it is reinforced by 4vol%BNNT, respectively.

The strengthening of Ti-xBNNT composite is mainly influenced by the dispersion of BNNTs at the grain boundaries and in-situ precipitated TiB phase within the grains and grain boundaries. Both of them make obstacles for the movement of dislocations and increases the strength by Orowan looping dispersion strengthening mechanism. When material is under applied stress, the dislocation starts to move and encounters dispersoids. The dislocation gets trapped by the pinning effect of dispersoids. At higher stress, the dislocation bows out, forms a loop, entangles each other and thus increases the strength of the composite [222]. Since BNNTs are a few microns long with nanoscale diameter, they are effective in blocking dislocation without shearing the nanotubes [62]. Moreover, a small contribution from solid solution strengthening might also take part in strengthening the composites. Oxygen, nitrogen and carbon atoms originating from raw Ti powder exist as interstitial atoms in the composite matrix. Besides, at higher sintering temperature BN dissolves to B and N atoms. The light N atom easily diffuses to the Ti matrix, occupies interstitial sites of the matrix and generates stress field in the lattice. These interstitial atoms form lattice distortion in titanium leading to strain localization. In the deformation process, this induced strain prevents movement of the dislocation and strengthens the composite. Oxygen content more than 0.25 wt% in titanium changes the slip deformation mode from wavy to planar and reduces twinning that increases the strength of the composite. Solute elements like Fe, Al, Mo, and V etc. from Ti powder and catalyst also form solid solution by substituting host titanium atoms in the matrix. The size misfit of these solute atoms also induces stress in the surrounding lattice that interacts with the movement of dislocation increasing the strength. Table 6.1 represents a comparison of mechanical properties between BNNT reinforced titanium matrix composites with other kinds of reinforcement.
Table 6.1: A comparison in the room temperature mechanical properties of TMC

<table>
<thead>
<tr>
<th>Composition</th>
<th>Processing Condition</th>
<th>Maximum Strength (MPa)</th>
<th>Yield Strength (MPa)</th>
<th>Failure strain (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>Ti-3wt%CNT</td>
<td>SPS + Extrusion + Annealing</td>
<td>670 (tensile)</td>
<td>520</td>
<td>33</td>
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<tr>
<td></td>
<td></td>
<td>920 (tensile)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiNi-5vol%CNT</td>
<td>HP (980°C, 1 h, 22 MPa)</td>
<td></td>
<td>90 (tensile)</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>HP (1050°C, 1 h, 22 MPa)</td>
<td>355 (tensile)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>HP (1120°C, 1 h, 22 MPa)</td>
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<td></td>
</tr>
<tr>
<td>Ti</td>
<td>Ti-30vol%TiB</td>
<td>HIP (1350°C)</td>
<td>670 (tensile)</td>
<td>690 (tensile)</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>Ti-5vol%TiB</td>
<td>VAR + MACS + HS</td>
<td>179 (tensile)</td>
<td>164</td>
<td>21</td>
</tr>
<tr>
<td>Ti</td>
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<td></td>
<td>787 (tensile)</td>
<td>639</td>
<td>13</td>
</tr>
<tr>
<td>Ti</td>
<td>Ti-15vol%TiB</td>
<td></td>
<td>902 (tensile)</td>
<td>706</td>
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<tr>
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<td>1734 (tensile)</td>
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<tr>
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<td>VAR</td>
<td>1462 (tensile)</td>
<td>23</td>
<td></td>
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<tr>
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<td>1412 (tensile)</td>
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<td>878 (tensile)</td>
<td>744</td>
<td>29</td>
</tr>
<tr>
<td>Ti</td>
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<td>CP + Sintering (800°C, 1h)</td>
<td>678 (compressive)</td>
<td>325</td>
<td>58</td>
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<td>650</td>
<td>19</td>
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</tbody>
</table>

SPS = Spark plasma sintering; HP = Hot pressing; HIP = Hot isostatic pressing; VAR = Vacuum arc remelting; MACS = Melt assisted combustion synthesis; HS = Hot swagging; RIM = Rapid infrared manufacturing; CP = Cold pressing

6.3.6 High Temperature Mechanical Properties

To realize the potentiality of BNNT reinforced titanium matrix composites in high temperature application, the mechanical properties of the manufactured composites were evaluated at 500°C. Fig 6.21 shows representative stress-strain curves for the composites after performing the compression test at the high temperature of 500°C. It seems that the strength of the composite is reduced as the flow stress increases at an elevated temperature. A higher amount of plastic deformation was also obtained in the composite than in the room temperature test. Pure Ti and composites having 0.5vol%BNNT content.
Figure 6.21: Stress-strain curve obtained from compression test at 500°C for composites sintered at (a) 800°C for 1 h (b) 1000° for 3 h (c) 1100° for 3 h and (d) 1200° for 3 h

Figure 6.22: High temperature (a) compressive strength and (b) reduction of length at fracture
showed no fracture of the sample. Similarly Ti-1vol%BNNT samples sintered at 800°C for 1 h and 1000°C for 3 h did not experience any fracture. The small fluctuations in the curves of Fig 6.21 appears due to the pores in the microstructure. At 500°C, when the composites are under continuous load, the pores are minimized resulting in slight drop in stress. The effect of high temperature on the compressive strength and ductility is shown in Fig 6.22. The compressive strength proportionally increases but ductility decreases with the increasing amount of reinforcement in the composite. Pure Ti bulk sintered at 800°C for 1 h has compressive strength of 112 MPa. This strength reaches to as high as 277 MPa with 5vol%BNNT reinforcement. The strength was improved by almost 150% because of nanotube reinforcement. The mechanical property enhancement is even much higher in the composites sintered at other conditions though not much differences could be observed. Pure Ti sintered at 1000°C, 1100°C and 1200°C shows a compressive strength of 135 MPa, 132 MPa and 138 MPa, which rises to 403 MPa, 413 MPa and 425 MPa with 5vol%BNNT reinforcement, respectively. The strength in these composites increased by 198%, 212% and 208% respectively. Moreover, unlike the room temperature compression test, the highest compressive strength was obtained in the Ti-5vol%BNNT composition irrespective of sintering conditions. The reduction of length at fracture on the other hand as shown in Fig 6.22b shows a good amount of deformation up to 29%, 38%, 36% and 33% for Ti-5vol%BNNT composite sintered at 800°C, 1000°C, 1100°C and 1200°C, respectively. At higher temperature softening of the material takes place by recovery and recrystallization process. In recovery process dislocations are annihilated in conjunction to the relaxation of induced strain at any mismatch. This increases the plastic flow and reduces the strength of the composites. But this high temperature softening process is inhibited by the presence of BNNT reinforcements and in-situ formed TiB phases resulting in increased strength in the composites. In contrast to the room temperature compression test, the composite sintered at 800°C showed less deformation at high temperature relative to the composites sintered at 1000°C, 1100°C and 1200°C. This phenomenon might be as a result of boron nitride nanotubes acting as reinforcement in the composites. Nanotubes at high temperature are more effective to transfer the load from matrix to the reinforcement. BNNTs may also be more effective in restricting high temperature softening process and grain boundary sliding during deformation process than the TiB phase. In BNNTs, the intra-layer bonding between B and N is governed by strong covalent bond and this resists deformation under shearing. Besides, a thin layer of
reaction phase may be form at the interface between Ti and BNNTs at 800°C sintering temperature, which makes stable bonding for effective load transfer within the composite, resulting in less plastic deformation. This implies that nanotube reinforced composites are suitable for high temperature applications. Table 6.2 compares the high temperature compression test properties of BNNT reinforced composites with other types of reinforcements.

Table 6.2: A comparison in the high temperature mechanical properties of TMC

<table>
<thead>
<tr>
<th>Composition</th>
<th>Processing Condition</th>
<th>Maximum Strength (MPa)</th>
<th>Yield Strength (MPa)</th>
<th>Failure Strain (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>SPS + Exrusion + Annealing</td>
<td>180 (tensile, 400°C)</td>
<td>170</td>
<td>24</td>
<td>[147]</td>
</tr>
<tr>
<td>Ti-3wt%CNT</td>
<td>SPS (800°C, 50 MPa, 5 min, 100°C/min)</td>
<td>140 (compressive, 600°C)</td>
<td>-</td>
<td>-</td>
<td>[144]</td>
</tr>
<tr>
<td>Ti-3wt%CNT</td>
<td>SPS (900°C, 50 MPa, 5 min, 100°C/min)</td>
<td>118 (compressive, 600°C)</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Ti-3wt%CNT</td>
<td>SPS (1000°C, 50 MPa, 5 min, 100°C/min)</td>
<td>132 (compressive, 600°C)</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>HIP (1350°C)</td>
<td>170 (Tensile, 400°C)</td>
<td>-</td>
<td>-</td>
<td>[64]</td>
</tr>
<tr>
<td>Ti-30vol%TiB</td>
<td>CP + Sintering (800°C, 1h)</td>
<td>112 (compressive, 500°C)</td>
<td>60</td>
<td>-</td>
<td>Ours</td>
</tr>
<tr>
<td>Ti</td>
<td>CP + Sintering (1000°C, 3h)</td>
<td>135 (compressive, 500°C)</td>
<td>73</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Ti-5vol%BNNT</td>
<td>CP + Sintering (1100°C, 3h)</td>
<td>132 (compressive, 500°C)</td>
<td>82</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>CP + Sintering (1200°C, 3h)</td>
<td>138 (compressive, 500°C)</td>
<td>87</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
| SPS = Spark plasma sintering; HP = Hot pressing; HIP = Hot isostatic pressing; CP = Cold pressing
6.3.7 Fracture Surface of Composites

The distribution of nanotubes, TiB whiskers and their effect on strengthening the composite was analysed by visualizing the fracture surface of the composite. SEM fracture images of Ti-5vol%BNNT composite sintered at various conditions are shown from Fig 6.23 to Fig 6.25. Fractography of Ti-5vol%BNNT composite sintered at 800°C for 1h as represented in Fig 6.23 shows ductile type failure as confirmed by the presence of elongated grains and the formation of shear bands in the matrix (Fig 6.23a). Fracture of the sample proceeded at around 45° angle to the vertical loading. Boron nitride

Figure 6.23: Fracture surface of Ti-5vol%BNNT composite sintered at 800°C for 1 h; (a) ductile type fracture (b) low magnification image showing segregation of BNNTs (c) a cluster of BNNTs (d) BNNTs reacted in a few places (e) protruded BNNTs from the matrix after fracturing of composite (f) fragments of BNNTs in the matrix
nanotubes were uniformly distributed in the Ti matrix as can be seen from the dark region of the microstructure in Fig 6.23b. A cluster of nanotubes was also observed in many places of the fractured sample as marked by circles. These nanotubes are located deep inside the craters. The Ti powders used for fabrication of composites was porous in nature and these BNNTs filled the void spaces during mixing process. Segregation of BNNTs also occur because of the irregular shape of starting Ti powders and large differences in sizes between Ti powder (<150 µm) and BNNTs (~2 µm). The nanotubes in agglomerated form (Fig 6.23c) tends to fill the interstitial spaces within the Ti powders, though lots of BNNTs were also seen on the Ti particle surface. The long BNNTs and their structural integrity in the fracture surface demonstrates that the nanotube is able to withstand a high pressure during the consolidation of the powders. A small fraction of *in-situ* formed TiB was also observed in a few places in cluster form (Fig 6.23d) as confirmed by the weak peaks of TiB phase in XRD. The synthesis and processing of BNNTs were accompanied by nanoparticles adhered to the nanotubes. It is believed that these nanoparticles preferentially reacted with Ti to form TiB in the early stages of sintering. Formation of interconnected TiB cluster takes place when their growths in multiple direction are intercepted to each other. Under deformation a micro void starts to form and multiplies. The pores, nanotube cluster, interface act as stress concentrator to form micro voids under loading. As the deformation is in progress, the crack starts to initiate at these voids by particle debonding and propagates along the grain boundary. The effectiveness of boron nitride nanotube in strengthening the composite is validated by the presence of protruding BNNTs from the matrix (Fig 6.23e). This indicates that load was transferred effectively from the soft Ti matrix to the reinforced BNNTs. These nanotubes embedded in the matrix imposed resistance to plastic deformation and fractured during crack propagation (Fig 6.23f). No pull out of nanotubes was observed which supports the good interfacial bonding between Ti and BNNT. High magnification image of protruding BNNTs reveal a thin layer of coating on individual nanotubes.

The fracture surface of the Ti-5vol%BNNT composite sintered at 1000°C for 3 h is shown in Fig 6.24. Most of the BNNTs in contact with Ti were reacted and transformed to TiB phase. Fig 6.24a shows such an individual BNNT at the transitional stage the majority of which portion has already been transformed to TiB. Clusters of BNNTs were also observed in few places (Fig 6.24b) with outer layer being transformed to a cluster of TiB.
whiskers indicating that the sintering temperature and time was not sufficient to react all the nanotubes. The structure of TiB was long needle shape preferentially grown one dimensionally (Fig 6.24c). A variety in cross-sectional morphology of TiB from circular to polygon with number of steps were seen in the composites (Fig 6.24d). Axial growth of TiB is six times faster along [010] direction (i.e. the needle axis that has the lowest activation energy for diffusion path) than the transverse direction owing to the Ti and B containing planes and their higher density of stronger bonds leading to independent whiskers [64]. Usually coarse TiB has hexagonal cross-section mostly bounded by (100), (101), (001) and (101) planes. These planes occasionally decomposes into stepped
morphology bounded by (001) and (101) planes resulting a variation in the hexagonal cross-section [64]. The size, morphology and amount of in-situ formed TiB depends on the sintering condition and distribution of BNNTs. A study on in-situ formed TiB reinforced Ti composite [101] where TiB₂ particles were used as the source of B atom reveals formation of long TiB needles at lower volume fraction of TiB₂ particles. At lower volume fraction, the larger contact area between Ti and TiB₂ particles helps in faster diffusion of B atom. At higher volume fraction the diffusion process slows down and backward diffusion of Ti occurs associated with a slow diffusion of B atom in transverse direction resulting in coarse TiB formation. That means the distribution of reinforcement in the matrix determines the progress of the reaction and has an influence on the size and shape of the TiB whiskers [102, 105]. A mixed mode of brittle and ductile fracture took place depending on the concentration of TiB phase in the matrix. TiB is a strong material with elastic modulus of 371 GPa [8] compared to 110 GPa for Ti and did not experience fracture while under load. The formation of TiB is thermodynamically favourable and

Figure 6.25: Fracture surface analysis of Ti-5vol%BNNT composite sintered at (a,b) 1100°C for 3 h and (c,d) 1200°C for 3 h
chemically/mechanically stable even at high temperatures as a result of minimal residual stress associated at the matrix-reinforcement interface. Most of fibre just pulled out (Fig 6.24d) from Ti matrix resulting in cleavage failure. Fig 6.24e shows abrupt facets of Ti fragmented from the matrix caused by pull out of TiB needles. Ductile failure of the composite was observed (Fig 6.24f) in other places where lower fraction of TiB exist. Similar mixed mode fracture were also seen in the case of in-situ formed TiC particle reinforced Ti-6Al4V alloy composite [67]. However, unlike TiB whiskers the crack initiated with the fracture of TiC particles in those composites.

Identical pattern but more brittle manner of fracture was observed in the composite sintered at 1100°C and 1200°C. No boron nitride nanotubes were found suggesting that all of them have taken part in the reaction forming TiB whiskers. The high volume fraction of TiB and their high hardness in the composites rendered large cleavage fracture in the form of a trench as can be seen in Fig 6.25a. Higher magnification reveals chunks of Ti interweaved by TiB needles (Fig 6.25b) are dangling from rest of the matrix. Some spherical shape particles (Fig 6.25c) composed of agglomerated particles could also be observed which might be the remaining’s of reacted BNNTs. The presence of pores (Fig 6.25d) are clearly visible in the fracture surface as they did not go any deformation in compression test.

### 6.3.8 Transmission Electron Microscopy of the Composites

In order to identify and analyse the reaction phases, their distribution and mechanism of formation in the matrix, TEM observation was carried out on Ti-5vol%BNNT composites sintered at various conditions. Fig 6.26a shows a cluster of BNNTs in the composite after sintering at 800°C for 1 h. The outer portion of the BNNT cluster which is in contact with Ti matrix reacts with Ti and forms long needles of TiB in the Ti side. Corresponding elemental mapping obtained from EDX as shown in Fig 6.26 (b to f) indicates solid solution of N in α-Ti matrix along with some O and C atoms. Ti powder naturally contains N, O and C as impurities in the raw material. Nevertheless, the abundance of N in Ti matrix suggests dissolution of BNNT or BN nanoparticles at the interface and migration of N atoms in the matrix. It can be mentioned that the synthesized nanotube contained a small amount of nanoparticles from the synthesis process. It is believed that these nanoparticles will preferentially react with Ti prior to nanotubes resulting in TiB whiskers in the matrix. The amount of N solid solution in Ti matrix was quantified by an EDX area analysis in the region as marked by white rectangle in Fig 6.26a. The examination reveals a composition of 81at%Ti and 19at%N in that region. This overwhelming N atom was
partly diffused from the side of BNNT cluster. Performing identical analysis in another Ti matrix region that is far away from any TiB phase and/or BNNT cluster exhibited different composition with 92at%Ti and 7at%N including a small amount of Na, Cr and Fe. Therefore, the difference in the compositional analysis supports the concept of greater N solid solution in the Ti matrix adjacent to the embedded nanotubes relative to nanotube free regions.

The structures of nanotubes in that cluster is more obvious in Fig 6.27a. Their bamboo structure with a conical hollow section at the interior is still retained after thermal treatment. Catalyst particles as marked by arrows in the form of dark circular shapes (actually spherical morphology) were also seen in the cluster. These catalyst particles are usually located at the top of nanotubes. They serve as a seed for growing nanotubes from ball milled B powders during annealing and their size determines the diameter of the nanotube. The high resolution image of nanotube at point “P” near to a catalyst particle is shown in Fig 6.27b. The parallel fringes in the outer layers of nanotube are clearly visible and still remain intact. No distortion could be observed in those layers because of thermal shock. The absence of thermal stress at these fringes indicates that BNNTs are

Figure 6.26: EDX elemental mapping at Ti-BNNT interface in composites sintered at 800°C for 1 h; (a) bright field image and mapping of (b) Ti (c) B (d) N (e) O (f) C elements
stable at this sintering temperature of 800°C. The composition of BNNT cluster and catalyst particles were identified by analysing EDX elemental mapping on that region and the result is shown in Fig 6.27(c-f). The intensity from B and N elements confirms the chemical composition of nanotubes as boron nitride. The catalyst particle seems to be element Fe that comes from the catalyst used for nanotube synthesis. A very small amount of Ti is also associated that may appear from stainless steel balls and container used in milling operation for synthesis of nanotubes.

The cross-section of a fine TiB needle as observed in the composite is shown in Fig 6.28a. Its lamellar structure is developed as a result of stacking disorder along the needle axis [4]. The compositional analysis (Fig 6.28b) at this cross-section shows the presence of only Ti and B elements depicting it as a TiB phase. A line profile across a TiB whisker (Fig 6.28c) shows a gradual decline of Ti and N concentration along its transverse direction. The concentration of Ti and N is higher in the matrix but lowered in the TiB region while B concentration is higher compared to the matrix. Thus TiB phase is qualitatively evident in the composite sintered at 800°C for 1 h either from the reaction of nanotubes or nanoparticles. In addition to the retained BNNTs and TiBs in this composite, some partially reacted nanotubes were also observed in some places particularly in the void areas. Fig 6.28d represents one of such kind of reacted nanotube.
protruding from the matrix. The centre of a knot in the bamboo structured boron nitride nanotube usually remains hollow in the form of conical sections after synthesis. But in this case of reacted nanotube, a cylindrical shape having stacking disorder appears inside the nanotube partially filling its centre. This implies that after reaction has occurred between Ti and BNNT, the reaction phase TiB starts to grow at the interior of nanotube gradually consuming it. This mechanism is also supported by the fracture image of 6.24a that shows a peeled off nanotube containing a TiB needle evolving from inside of nanotube. The partially reacted nanotube as seen in Fig 6.28d seems at the early stage of growth.

Figure 6.28: (a) Cross-section of TiB (b) EDX area analysis in that cross-section (c) line profile across a TiB whisker (d) partially reacted nanotube
Fig 6.29a shows a TEM image of a TiB needle observed in the composite sintered at 800°C for 1 h. The longitudinal axis of a TiB representing the needle axis grows along [010] direction. This growth is faster than the growth of transverse direction. This faster growth of TiB along [010] direction bounded by the slowest growing facets forms a needle shape owing Ti and B containing planes and their higher density of stronger bonds in that direction. The high resolution image of the TiB needle in Fig 6.29b shows no stacking fault in the (100) plane. Stacking faults are common in the sintered composites as B diffuses towards [010] direction in Ti matrix [67]. Selected area diffraction (SAED) patterns obtained from Ti matrix and TiB in Ti matrix are represented in Fig 6.29c and Fig 6.29d, respectively. The hexagonal array in Fig 6.29c confirms its α-Ti phase while the overlapping streaking in Fig 6.29d appears both from α-Ti and TiB phase in the composite [104, 228]. The crystal structure of TiB is B27 orthorhombic (a = 6.12 Å, b = 3.06 Å, c = 4.56 Å) having a zig-zag chain of boron atom along the b-direction [100, 112]. It consists of trigonal prism where B atom lies at the centre surrounded by six Ti atoms. These trigonal prisms are stacked horizontally in a columnar array with two of its
rectangular faces connected each other depicting a zigzag B chain along the [010] direction i.e. the column. These columns of prisms are connected to each other at the edges forming a pipe like structure composed of Ti atoms having trapezoidal cross-section. Along the zig-zag chain of B atom in [010] direction each B has two nearest neighbours with an atomic distance of 1.88 Å. Considering atomic radius of Ti (1.475 Å) and B (0.87 Å), the largest possible channel diameter through which one B atom can jump from one site to its nearest site is 1.42 Å that represents one dimensional lowest activation energy path for diffusion of B atom in the needle direction.

Figure 6.30: (a) TiB phases in composites sintered at 1000°C for 3 h (b) partially reacted BNNTs (c) EDX line profile in partially reacted nanotube and (d) sectioned image of reacted nanotubes
Figure 6.31: (a) Bright field image of reacted nanotubes and EDX elemental mapping of (b) Ti (c) B (d) N (e) O (f) C

Figure 6.32: (a) Randomly oriented TiB in the composite sintered at 1100°C for 3 h and (b) formation of twins in the matrix
Figure 6.33: (a) Bright field image from the cross-section of a coarse TiB whisker and EDX elemental mapping of (b) Ti (c) B and (d) N; (e,f) diffraction pattern obtained from TiB cross-section (g,h) diffraction pattern from TiB and α-Ti matrix
As the sintering temperature was increased to 1000°C, most of the nanotubes were transformed to TiB by the reaction as can be seen from the TEM image of Fig 6.30a showing coarse and fine TiB whiskers randomly oriented in the Ti matrix in clustered form. Yet a number of partially reacted nanotubes were also observed in the region of pores (Fig 6.30b). Fig 6.30c shows an EDX line profile from a reacted nanotube which is partially transformed to TiB phase. As can be seen, the concentration of Ti was greatly increased at the centre of the nanotube. Though B and N concentration also increases in the core, much higher N concentration in the core compared to B concentration indicates that it was a boron nitride nanotube before the reaction. And after the nucleation of reaction phase at the interface it started to grow in the core section of the nanotube. Thus the EDX line scan distinctively compares the compositional difference between a fully formed TiB and partially formed TiB as shown in Fig 6.28c and Fig 6.30c, respectively. The sectioning of such kind of reacted nanotube (Fig 6.30d) most probably by ion milling demonstrates TiB needle at the core with outer layer being Ti coated BNNTs. An elemental mapping of partially reacted BNNTs as observed in Fig 6.30b further confirms simultaneous existence of TiB and BNNT together (Fig 6.31). The high concentration of Ti and B element in the core section justifies the presence of TiB phase while N is scattered both in the core and outer sections. TEM image from composites sintered at 1100°C for 3 h as shown in Fig 6.32a illustrates a similar pattern of randomly oriented TiB phase formed in the Ti matrix but neither any unreacted nanotube nor any partially reacted nanotube could be observed. A number of twins (Fig 6.32b) formed by stress concentration [147] are also observed in a few places which is common in Ti. Deformation of Ti also takes place through the twin mechanism.

Fig 6.33a shows a bright field image from the hexagonal cross-section of a coarse TiB whisker observed in the composite sintered at 1200°C for 3 h. Their cross-section is bounded by the slowest growing facets of (100), (101) and (101̅) planes [67, 115]. The high concentration of B in combination with moderate Ti concentration in the corresponding elemental analysis as shown in Fig 6.32(b-d) manifest it is the TiB phase. The mapping corroborates the line profile analysis as shown in Fig 6.28c. The diffraction pattern obtained from such kind of another cross-section is shown in Fig 6.33(e & f). This diffraction pattern from TiB was compared with the combined diffraction pattern obtained from both TiB and α-Ti matrix as displayed in Fig 6.33 (g and h). A point analysis (Fig 6.33j) on the outer surface of TiB needle (Fig 6.33i) also shows Ti and B
phase amounting to 55at%Ti and 45at%B, which can be roughly estimated as TiB concentration. The presence of dislocations in the matrix and their pile up against TiB needles were also observed in TEM as shown in Fig 6.34(a-c). These TEM samples were prepared from Ti-5vol%BNNT composites after deformations during the compression test. The dislocations are generated as a result of deformation process and their movement is prevented by the pinning effect of grain boundaries, BNNTs and in-situ formed TiB needles. Consequently, they pile up around the obstacles and strengthen the composites.

Figure 6.34: Interactions with dislocations for strengthening the composites obtained from deformed samples; (a) presence of dislocations in the matrix; TiB-dislocation interactions in the composites sintered at (b) 1000°C for 3 h and (c) 1100°C for 3 h
6.3.9 Effects of h-BN and BNNT Reinforcements

Comparing the effect of h-BN particles and BNNTs on the microstructure and mechanical properties shows they have similar effect on the density and grain refinement of the composites. However, the mechanical properties of h-BN and BNNT reinforced composites are quite different, as can be seen from Fig 6.35 that compares maximum compressive strength and corresponding reduction of length data obtained in these composites. The composites of Ti-5vol%BN sintered at 800°C exhibited a superior compressive strength of 1013 MPa relative to 985 MPa obtained from the Ti-4vol%BNNT composite. But BNNT reinforced composite exhibited better ductility than h-BN reinforced composites. As the in-situ formed TiB phase forms in the composite at higher temperatures like 1000°C, 1100°C and 1200°C, the BNNT reinforcement gives higher strength than h-BN reinforcements along with good amount of ductility. The good ductility of BNNT reinforced composites enables them suitable for further hot working processes (e.g. hot rolling, extrusion) to improve the mechanical properties further. In addition, another distinguishing feature was also observed in the composites sintered at 1000°C for 3 h. Fracture surface observation of the h-BN particle reinforced composite sintered at this condition showed no existence of h-BN particles in the matrix, while a small amount of BNNTs remained under the same sintering condition. Although the exact TiB volume fractions in these composites are still unknown, qualitative analysis indicates that h-BN particles are more prone to react with Ti compared to BNNTs. This means BNNTs are much stable as reinforcements than h-BN particles in Ti composites.

Figure 6.35: Comparison of maximum strength and corresponding ductility for h-BN and BNNT reinforced composites; (a) Compressive Strength (b) Reduction of Length
6.4 Conclusion

Boron nitride nanotube reinforced titanium matrix composite was successfully manufactured by conventional pressing and sintering techniques. BNNTs were found uniformly distributed in Ti matrix though agglomerated BNNTs were also observed in many places. This happened because of large differences in sizes between Ti and BNNTs where BNNTs tends to fill the void spaces within Ti powders. A high density in the range of 95-97% was obtained in the sintered composites along with formation of TiB phase. The in-situ formed TiB phase appears in the matrix by the reaction between Ti and BNNTs and their proportion increases as the sintering temperature is increased with a simultaneous decrease in the amount of reinforced nanotubes. Therefore, BNNTs were effective as reinforcement when composites were sintered at 800°C for 1 h. After sintering at 1000°C for 3 h, a small fraction of BNNTs remained while the TiB phase dominates in the composite. No BNNTs were found in the composite sintered at 1100°C and 1200°C implying that all of them were transformed to TiB phase. Incorporation of BNNTs in the Ti matrix refined the grain size of the composite and the grains became equiaxed, though microstructure contains higher amount of pores with higher amount of reinforcement. On the other hand, the sintering condition showed not much effect on grain size and its morphology. Grain refinement, equiaxed morphology and greater amount of pores is mainly caused by the restricted diffusion process as a result of nanotube reinforcement.

Compression tests both at room temperature and 500°C showed a significant increase in the mechanical properties of the composites. The highest room temperature compressive strength was obtained for the Ti-4vol%BNNT composites, while the 5vol%BNNT reinforced composite exhibited the highest compressive strength at 500°C irrespective of sintering temperature and periods. Unreinforced pure Ti sintered at 800°C for 1 h showed a room temperature compressive strength of 678 MPa and this strength reaches to a maximum of 985 MPa by 4vol%BNNT reinforcement. This increased strength is mainly contributed by BNNTs. An increase in strength up to 1330 MPa was obtained from the combination of reinforced BNNTs and in-situ formed TiB when composites were sintered at 1000°C for 3 h. The highest strength of 1421 MPa comes from the composite sintered at 1100° for 3 h which is delivered only by in-situ formed TiB whiskers. Likewise Ti-5vol%BNNT composite sintered at 800°C showed a maximum compressive strength of 277 MPa at the 500°C compression test. For the same composition, this strength increases to 403 MPa, 413 MPa and 425 MPa when composites were sintered at 1000, 1100 and
1200°C for 3h, respectively. Contrary to room temperature ductility, composites sintered at 800°C showed the lowest ductility at the high test temperature. This might be as a result of greater resistance to plastic deformation by the dominating BNNTs in those composites. Fracture surface exhibited mixed mode of ductile and brittle fracture in the composites depending on the location of BNNTs and TiB in the matrix. Elongated grains and intergranular fracture were observed in the portion where less reinforcement existed. In contrast, highly brittle and transgranular cleavage type fracture occurred in the places where BNNTs and TiB reside in a clustered form.

The identification, distribution and mechanism of formation of BNNTs, in-situ formed TiBs were systematically analysed in the TEM. BNNTs retain their structural integrity in the composite sintered at 800°C despite a few TiB whiskers along with partially reacted BNNTs could be observed. Composites sintered at 1000°C showed an abundance of TiB formation in the Ti matrix with a small fraction of partially reacted BNNTs at the voids. After nucleation of reaction phases at the Ti-BNNT interface they start to grow first on the inner side of the nanotube consuming nanotube walls and then grow along the longitudinal direction consuming the rest of the nanotube. A high concentration of N solid solution in the Ti matrix region adjacent to the nanotube manifest N diffusion after reaction has occurred. Compared to other kinds of reinforcements BNNTs are effective in reinforcement for room and high temperature applications.
7 Interfacial Reaction between Titanium and Boron Nitride Nanotubes

7.1 Introduction

The fabricated BNNT reinforced Ti matrix composite in the previous chapter (chapter 6) demonstrated improved mechanical properties both at room and high temperature compared to pure Ti bulks. This enhanced mechanical properties can be attributed to the distributed BNNTs and TiB whiskers in the matrix depending on the sintering conditions. BNNTs are dominant in the composites sintered at lower temperatures like 800°C. At this temperature a slight reaction between Ti and BNNT occurred as observed from the fracture surfaces (Fig 6.23d). It seems that these reaction phases are in their initial states and their morphologies are not clear. They exist at the Ti-BNNT interface and mostly distributed in the grain boundaries. However, when composites were sintered at 1000°C, majority of BNNTs reacted with Ti resulting in fully formed TiB whiskers in the matrix which are clearly visible at the fracture surfaces (Fig 6.24 (c and d)). These TiB whiskers are randomly oriented and distributed in the matrix within the grains and grain boundaries. Therefore, depending on the sintering temperature it is obvious that the kind of reaction products, their distribution and morphologies in Ti-BNNT composite are in different forms. Their variations also strengthened the composite in different manner.

It has been found that reactions between reinforcement and matrix material during thermo-mechanical processing of composites impose a significant effect on the final properties of the composite [97, 100]. In composite, load transfer from the soft Ti matrix to the harder ceramic reinforcing agents takes place by shear stress at the interface. If the interface is not stable, load will not be transferred effectively and catastrophic failure may occur. A thin reaction zone (<20nm) may be beneficial as it enhances the bonding and good for mechanical properties [62]. But a thick reaction layer (>100nm) at the interface has detrimental effect leading to catastrophic failure [63].

Previously the interfacial reaction products between Ti and BN has been investigated [84-86] by sintering BN plates in Ti powders at the temperature range of 1000~1200°C in vacuum for various holding time. The phase sequence was found to be BN–TiB₂–TiB–
TiN\textsubscript{1-x}–Ti\textsubscript{2}N-\alpha Ti(N). In another investigation [87] composites sintered at 1000°C, 1400°C and 1600°C revealed the phase sequence as Ti/\alpha Ti-\alpha Ti(Ti\textsubscript{2}N)-\alpha Ti(Ti\textsubscript{2}N)/TiB-TiB/Ti\textsubscript{3}B\textsubscript{4}-Ti\textsubscript{3}B\textsubscript{4}/TiB\textsubscript{2}-TiB\textsubscript{2}/BN. But none of those explained the mechanism of TiB formation in the matrix.

Therefore, it is of great interest to analyse the nucleation of initial reaction phases at Ti-BNNT interface, their subsequent growth mechanism and how their morphology changes to TiB whiskers with respect to temperature and time. This would help to explain the strengthening mechanism imparted by the reaction products, tailoring the microstructure and controlling the mechanical properties of the composites. In this chapter, titanium coated boron nitride nanotube nanocomposite was fabricated by sputtering process and their interfaces were investigated for a wide range of heat treatment temperature and time.

### 7.2 Experimental

Starting boron nitride nanotubes were synthesized by ball milling and annealing method using boron powders in a specially designed rotating furnace as discussed earlier in chapter 4. A small quantity of as-synthesized boron nitride nanotubes were first ultrasonicated in ethanol for proper dispersion in the solvent. The nanotube containing solvent was then dropped on the hot surface of silicon wafer substrate heated in a hot plate and kept it for a while. Once the ethanol is evaporated boron nitride nanotube dispersed silicon wafer was placed on a disc and inserted into the sputtering chamber to deposit titanium film on the surface of nanotubes according to the sputtering conditions as shown in Table 3.3. The thickness of coating varies depending on the applied power and sputtering time. The titanium coated boron nitride nanotubes were then heat treated in a temperature range of 500–1200°C for different holding time from 10 min to 3 h.

These heat treated samples were then investigated to understand the reaction mechanism and reaction product formation between titanium and boron nitride nanotubes.

X-ray diffractometry (XRD) analyses of the heat treated nanocomposites were conducted in a PANalytical X’pert Pro MRD XL machine using Cu\textalpha radiation (0.154056 nm) in a 2\theta range of 10–110° applying 40 kV and 30 mA. Morphology of the heat treated nanocomposites were observed by scanning electron microscope (SEM) using a Zeiss Supra 55 VP FEG SEM. Transmission electron microscopy (TEM) of the heat treated nanocomposite samples were conducted in a JEOL 2100 FEG TEM to obtain high resolution electron image and diffraction patterns.
7.3 Results and Discussion

7.3.1 Nucleation, Growth and Morphology of Reaction Products

SEM images of as sputtered Ti coated BNNTs are shown in Fig 7.1 (a & b). Ti coating on the dispersed nanotubes was homogeneous though the thickness of coating is unknown. It can be assumed that the coating was very thin in nanometre scale as the knots and joints of nanotubes are still clearly visible in the coated nanotubes but the hollow conical section inside them could not be observed. The reason is thin Ti coating wrapped around the nanotube surface thoroughly. The heat treated samples at 500°C, 600°C and 700°C for 1 h demonstrated similar kind of morphology without affecting the structure of nanotubes. This indicates that nanotubes are stable at these high temperatures with titanium. However, a disturbance on the nanotube structure was observed when they are heat treated at 800°C for 1 h as shown in Fig 7.2. It seems that the outer surface of nanotube was severely affected than the inner side of nanotubes. It can be assumed that the outer portion of nanotube which is in direct contact with titanium have already been reacted with Ti and formed these particles on the nanotube surface while rest of the parts of nanotube still remain intact. This is evident in the region of agglomerated nanotubes (Fig 7.2a) on the substrate that exhibited unreacted nanotubes underneath the reacted ones as Ti coating could not reach in those nanotubes homogeneously. That’s why the analysis was mainly performed on the individually dispersed nanotubes (Fig 7.2b) rather than the agglomerated one since this would show the exact behavioural pattern. Some ultrafine particles were also grown on the outside shell of nanotubes at different locations as can be seen from the bright spots on the surfaces (Fig 7.2(c and d)). Most probably these ultrafine particles belong to the reaction product which is still in progress.

The reaction turns into severe manner in the composites heat treated at 900°C for 1 h as shown in Fig 7.3a. At this higher temperature, the reaction product has been grown into bigger size by consuming adjacent sections of nanotube and this caused sectioning of nanotubes in different places along its length (Fig 7.3(b and c)). The morphology of the reaction product in these 800°C and 900°C heat treated samples are mainly plate like but they exist in the form of two distinctive shape: elongated and hexagonal prism like (Fig 7.3d).
Figure 7.1: SEM images of (a, b) Ti coated BNNTs and heat treated at
(c, d) 500°C for 1 h (e, f) 600°C for 1 h (g, h) 700°C for 1 h
The phases formed by the heat treatment were analysed by XRD and the XRD pattern is shown in Fig 7.4. The main peak for boron nitride phase is obvious as it appears at around 26.75° corresponding to the hexagonal crystal structure from (002) plane. A small peaks from TiB and α-Ti phases are also evident in the XRD pattern along with stronger peaks from the substrate. At 700°C temperature, the intensity from (002) plane of nanotube is very high and sharp indicating structural integrity of the nanotubes. However, a reduction of peak intensity at 800°C and 900°C implies a disorder in the nanotube structure because of the reactions. On the other hand, peak from TiB phase becomes stronger as the heat treatment temperature rose indicating much more TiB phase formation in expense of BNNTs. The α-Ti peak in the 800°C treated samples becomes distinctive as a result of recrystallization process. At this temperature they turn into more crystalline structure which is then starts to decay at 900°C by taking part in the reactions. It can be mentioned that the BNNTs contained a small amount of nanocrystalline particles formed during the synthesis process which may preferentially react with Ti to form TiB. This might be the reason for the appearance of TiB phases in the XRD pattern obtained from 700°C treated sample though no reaction phases could be observed in the SEM image (Fig 7.1h).

Figure 7.2: SEM images of Ti coated BNNTs heat treated at 800°C for 1 h; (a) low magnification image of agglomerates (b) reaction particles formed on the surfaces of BNNTs (c & d) formation of nanocrystalline particles
Figure 7.3: SEM images of Ti coated BNNTs heat treated at 900°C for 1 h; (a) low magnification image of nanotube clusters (b & c) consumption of nanotube by reaction caused sectioning of nanotube at different locations (d) elongated and hexagonal prism like particles formed as a result of reaction

Figure 7.4: XRD patterns obtained from the heat treated nanocomposites
To identify the onset of reaction, Ti coated BNNT nanocomposites were heat treated at 800°C for 10 min and 30 min, and the resulting SEM images are shown in Fig 7.5. A slight change on the nanotube surface structure was observed after 10 min heating (Fig 7.5b). It seems that titanium nanoparticles starts to form into grains at this temperature by recrystallization process and the grain size increased as the heating continues up to 30 min leading to rigorous effect on the surface of nanotubes (Fig 7.5c). And the effect is not only clearly visible on the nanotube surface but also on the substrate as well (Fig 7.5d). Transmission electron microscopy of the nanocomposites samples heat treated at 800 for 30 min as shown in Fig 7.6 demonstrates that nucleation of reaction phases occurred at different locations on the surface of nanotubes despite bamboo structure of nanotube including hollow conical section inside them are still intact. This is evident by the presence of dark spots on the nanotube surface as can be seen in Fig 7.6a. It seems that the reaction is uneven as their formation and distribution varied throughout the nanotube surface. Most of them are in the premature state might be nucleated but not grown enough. High magnification image in Fig 7.9b manifests no lattice disturbance occurred on the nanotube walls as a result of thermal treatment. The inset shows diffraction pattern obtained from the nanotubes. The image also shows a thick amorphous
layer with approximately 5 nm sizes surrounding the outer shell of nanotubes. This layer could be formed as a result of nitrogen atom diffusion towards the Ti coating. The nucleation and growth of reaction phase is dependent on the reaction kinetics between the participating compounds. However, a large crystalline reaction product which was grown sufficiently can be observed at the joint of bamboo shaped structure as marked by arrow in Fig. 7.6a. Knots of bamboo structured nanotube are highly prone to react faster than the other regions [63]. This is due to the dangling bond and interlocking compressive strength at the joint between two adjacent stems. High resolution image from this nanocrystal (Fig 7.6c) shows its elongated shape with 41 nm long and 23 nm wide roughly. Calculation of lattice spacing (0.327 nm) from this high resolution image represents (001) plane from hexagonal TiB$_2$ crystal structure (Fig 7.6d). At high temperature, nitrogen is released by the reaction between Ti and B. The smaller nitrogen atom diffuses towards titanium and

Figure 7.6: TEM images from the composites heat treated at 800°C for 30 min; (a) nucleation of reaction phase on the nanotubes (b) high magnification image from the outer walls of nanotube (c) high magnification image of the nucleated reaction phase as marked by arrow in the first picture (d) calculation of lattice spacing from the high resolution image of the nucleated phase
forms solid solution. On the other hand, the reaction between Ti and B results in TiB$_2$ or TiB phase. The whole process is driven by the dissolution of nitrogen in titanium and the kind of reaction product formation is dependent on the concentration of Ti and BN compounds [83]. At lower BN concentration the reaction can be shown as

$$2\text{Ti} + \text{BN} = \text{TiN} + \text{TiB} \quad (7.1)$$

However, an increase in the BN content reduces the amount of TiB as a result of formation of TiB$_2$ by the following reaction

$$3\text{Ti} + 2\text{BN} = 2\text{TiN} + \text{TiB}_2 \quad (7.2)$$

In the case of nanocomposites the local concentration of Ti is much less compared to the BN phase in nanotubes. Therefore, the initial formation of TiB$_2$ crystals by the reaction is also valid according to the Ti-B binary phase diagram [55] which shows TiB forms till 18wt% B concentration and TiB$_2$ forms above 30wt% B content.

The distribution and growth alignment of these nucleated reaction phases are more obvious in the TEM observation of the samples heat treated at 800°C for 1 h as shown in Fig 7.7. It shows that TiB$_2$ crystals were nucleated just on the surfaces of nanotube and then grown radially inside the nanotube gradually consuming the inner portion of nanotube (Fig 7.7a). The arrow marks in Fig 7.7a indicates nucleation of TiB$_2$ crystals on the other side of nanotube. It seems that the amorphous layer on the outer shell of nanotube also increases to around 13 nm with the longer exposure time though internal structure of nanotube retains their integrity (Fig 7.7b). A high magnification image from one of the TiB$_2$ crystals nucleated and grown on the nanotube surface (Fig 7.7c) shows that the amorphous layer is also present around the TiB$_2$ crystals. This large crystal with 33 nm long and 15 nm wide is slightly elongated and consumed almost half of the BNNT wall. An interfacial mismatch between BNNT and TiB$_2$ crystal boundaries could be observed in the high resolution TEM image (Fig 7.7d) might be due to growth pattern of TiB$_2$ crystals. The lattice spacing of both BNNT and TiB$_2$ side was calculated from the high resolution TEM image. The lattice spacing in the BNNT region was found to be 0.164 nm corresponding to (004) plane for hexagonal boron nitride. In contrast, the calculated lattice spacing at the TiB$_2$ side was 0.184 nm which corresponds to the (301) plane for TiB phase. This implies that TiB$_2$ crystal are partially transformed to TiB phase.
at longer heat treatment conditions as more Ti from the surroundings migrate and take part into the reaction. Similar findings were also observed in the investigation of TiB$_x$ coated SiC fiber reinforced Ti-6Al-4V composites [100]. The high concentration of B at the TiB$_x$ side diffuses towards Ti to form TiB$_2$ at first and then TiB at the Ti-TiB$_2$ interface. The formation of TiB$_2$ was a transition phase at the boron rich side that disappeared at longer annealing period providing B for further TiB formation. Moreover, a study on Ti-BN interfacial system [84-86] sintered at 1000~1200°C for various holding time in vacuum also resulted in TiB$_2$ phase at the BN rich side and TiB phase at the Ti side.

The crystal structure of TiB is B27 orthorhombic and TiB$_2$ is C32 hexagonal but both of them are consisting of trigonal prism stacked in different way where boron atom lies at the centre surrounded by six Ti atoms [100, 112]. B27 crystal structure forms by horizontal stacking of prism in columnar array with two of its rectangular faces connected each other depicting zigzag B chain along [010] direction i.e. the column. These column of prism are connected to each other at the edges forming pipe like structure composed
of Ti atoms having trapezoidal cross-section. In contrast, trigonal prisms are vertically stacked in a closed packed manner to have alternate planes of Ti and B atom along the c-direction in TiB₂ crystals. TiB₂ crystals are multifaceted with some of its face pertaining to slowest growth kinetics [229]. The facet {0001} is well developed and has the largest surface area compared to {01\overline{1}0} facets. Other pyramid like face {1\overline{1}01} and prismatic {1\overline{1}20} face could also be observed in these TiB₂ crystals. The slowest growth along (0001) and {1\overline{1}00} and fastest growth along {1\overline{1}20} leads TiB₂ crystal to two dimensional

Figure 7.8: Dark field TEM images from the nanocomposites heat treated at 800°C for 1 h; (a, b) low and (c, d) high magnification images
growth into plate like morphology. Calculation of thermodynamic data in a previous study shows that although TiB$_2$ has the lowest negative free energy of formation, Ti and TiB$_2$ can further react to form TiB due to the small negativity of the free energy [105]. This means that despite TiB$_2$ can form first upon reaction between Ti and B on the B-rich side, this TiB$_2$ would eventually convert to TiB as long as the B concentration in the reaction zone is less than 18 to 18.5%.

The morphology of TiB$_2$ crystals and its orientation with nanotube surface is more conspicuous in the dark field TEM images as shown in Fig 7.8. Low magnification images show (Fig 7.8a & Fig 7.8b) numerous TiB$_2$ crystals formed on the surface of nanotubes particularly on the nanotubes which were directly in contact with Ti coating. High magnification image (Fig 7.8c & Fig 7.8d) show plate like TiB$_2$ morphology consisting two large surfaces opposite to each other and few small surfaces across these large surfaces. The large surfaces corresponding to {0001} plane nucleates aligned to the nanotube surface. Similar kind of alignment was also observed where (0001) plane of TiB$_2$ crystal is oriented in parallel to (110) plane of NiAl matrix [230]. The schematic diagram in Fig 7.9 explains the TiB$_2$ crystal orientation with respect to BNNTs at their interface. Such TiB$_2$ crystals and their orientation with BNNT is also clearly evident in the SEM image of Fig 7.3d.

![Figure 7.9: Schematic diagram of (a) TiB$_2$ crystal morphology and (b) its orientation alignment after nucleation on BNNT surface](image.png)
The reaction between Ti and BNNT proceeds as a function of time and temperature. At much higher temperatures and longer sintering periods all the BNNTs dissolve and only TiB and TiB₂ reaction product retains as residual. And this can be seen clearly in the SEM images of the composites heat treated at 1000, 1100 and 1200°C for 3 h as shown in Fig 7.10. It shows needle like TiB whiskers and plate like TiB₂ particles remaining on the substrate. When nanocomposites were heat treated at these higher temperature, most of the enclaved TiB₂ crystals grow elongated manner as soon as they comes into contact with more Ti from the surroundings. In this case Ti coating on the substrate provided further Ti supply for reaction. As the reaction proceeds, B atom starts to diffuse towards

Figure 7.10: SEM images of the nanocomposites after heat treatment at (a,b) 1000°C for 3 h (c,d) 1100°C for 3 h and (e,f) 1200°C for 3 h
[010] direction turning TiB$_2$ plates into TiB needles as can be seen from Fig 7.10b. Whereas some of the TiB$_2$ plates could not be transformed into TiB needle due to insufficient local Ti concentrations. This explains that TiB$_2$ crystals form at the beginning of Ti and BNNT reaction which is a transitional phase and this phase is transformed to TiB phase at the exposure of higher temperatures and longer holding periods provided that sufficient Ti is available to take part into reactions.

### 7.3.2 Effect of Reaction Products on the Mechanical Properties

The investigation of various heat treatment conditions on the Ti coated BNNT nanocomposite revealed nucleation of TiB$_2$ crystals at their interface when heat treated at 800°C for 30 min. With a longer period of exposure up to 1 h, these nucleated particles grow into particle form on the nanotube surface. Comparing this phenomenon with the bulk BNNT reinforced Ti matrix composite as manufactured in chapter 6 indicates that formation of TiB$_2$ crystals at the Ti-BNNT interface stabilize the bonding between Ti matrix and BNNT reinforcements. Since the reinforced BNNTs are located at the grain boundaries, the as grown TiB$_2$ particles would also exist at the grain boundaries. Therefore, the load applied to the composites will be transferred smoothly from the soft Ti matrix to the reinforcing BNNTs through TiB$_2$ phases. Besides the strength imparted by the TiB$_2$ crystals at Ti-BNNT interface would prevent grain boundary sliding in the composites under shear deformation resulting in high temperature strength of the composites.

On the other hand, nanocomposites heat treated at higher temperatures like 1000°C or above exhibit no interfacial reaction phases. In those cases Most of the BNNTs dissolve and react with Ti forming *in situ* TiB whiskers randomly oriented in Ti matrix. These TiB whiskers has no role on delivering load transfer from Ti matrix to the reinforcing BNNTs rather they act as the reinforcement in the composite like BNNTs and strengthen the composite by dispersion hardening mechanism.

### 7.4 Conclusion

Ti coated boron nitride nanotube nanocomposite was successfully synthesized by sputtering process. The interfacial reaction pattern between Ti and BNNTs were systematically investigated by conducting various heat treatment conditions. Boron nitride nanotubes are able to withstand till 700 °C with their structural integrity without
reacting to Ti. Recrystallization of as sputtered Ti starts at 800°C with 30 min exposure time. This recrystallization process in conjunction with diffusion process activates the reaction between Ti and BNNT leading to the nucleation of TiB$_2$ nanocrystals throughout the surface of nanotubes. They nucleate aligning their $\{0001\}$ plane parallel to the nanotube surface which is the largest and slowest growing face of TiB$_2$ crystals. With a higher exposure time up to 1 h, TiB$_2$ nanocrystals grow more into longitudinal direction (direction towards nanotube axis) but less in transverse direction (i.e. radial direction of nanotube) consuming outer shell of nanotubes and becomes plate like morphology. At this stage TiB$_2$ crystals are partially transformed to TiB phase as more Ti from the surroundings migrate and takes part into the reaction. The formation of TiB$_2$ crystals at the Ti-BNNT interface is helpful in stabilizing the bonding between Ti matrix and BNNT reinforcements. The exposure of higher temperatures like 1000°C or above cause faster diffusion of B atom towards [010] direction transforming most of the TiB$_2$ crystals into TiB needles. TiB$_2$ crystals which are in lack of Ti concentration remain as TiB$_2$ plates without transformation. Unlike TiB$_2$ crystals, TiB needles increases the strength of the composite as a result of in-situ reinforcements.
CHAPTER EIGHT

8 Conclusion

A specially designed rotating furnace was used to produce large quantities of high density BNNTs using the ball milling and annealing method for Ti composites. The synthesis process was optimized under various annealing conditions, powder insertion temperature, tilt of the furnace and gas flow rates, in order to obtain nanotubes with a high aspect ratio. Annealing the ball milled boron powders at 1200°C for 3 h in the rotating furnace was found to give a higher yield of nanotubes than that of a conventional horizontal tube furnace. The yield of nanotubes was even higher when the ball milled powder was inserted at high temperatures (i.e. at 1200°C). Under these conditions, the nanotubes were \( \sim 5 \mu \text{m} \) long and \( \sim 90 \) nm in diameter. When the steel balls were mixed with the ball milled powder for improved rolling performance, the density of the synthesized nanotubes was increased but the nanotubes became coarse and thick. The largest quantity of dense nanotubes was obtained when the annealing was performed at 1200°C for 1 h at a gas flow rate of 4 L/min, because the strong gas flow effectively suspended the fine powder inside the furnace. However, the rolling of powder inside the furnace caused the synthesized nanotubes to agglomerate.

In order to understand the effect of particle reinforcement on the microstructure and mechanical properties of the composite, hexagonal boron nitride (h-BN) particle reinforced Ti matrix composite was prepared using the conventional pressing and sintering method. The h-BN particles were uniformly distributed in the composites by short-time ultra-sonification followed by ball milling. A high density in the range of 95\text{-}97\% was obtained in the composite after sintering at different conditions. The reinforcement in the composite reduced the grain size but rendered higher amounts of pores in the microstructure. According to the fracture surface, the structure of h-BN particles remained intact at lower sintering temperature of 800°C for 1 h. An increase in sintering temperature to 1000°C resulted in the formation of TiB phase in the composite, along with a smaller fraction of retained h-BN particles in the matrix when composites were sintered for 1 h. However, no h-BN particles could be observed in these composites when they are sintered for longer periods up to 3 h. A higher sintering temperature of 1100°C and 1200°C resulted in a similar microstructure. Evaluation of the hardness tests of the composites demonstrated proportional increases in Vickers hardness with the
content of reinforcements and sintering temperatures increased. The composite Ti-5vol%BN sintered at 800°C for 1 h showed the maximum room temperature compressive strength of 1013 MPa. On the other hand, the highest compressive strength of 1470 MPa was obtained from the Ti-3vol%BN composite which was sintered at 1200°C for 1 h.

The nanotube synthesized from the rotating furnace was employed to fabricate BNNT reinforced Ti matrix composites by a similar pressing and sintering method. BNNTs were uniformly distributed within Ti powders without affecting their structural integrity by performing a short duration of ultrasonification followed by a gentle ball milling operation. A high density, in the range of 95~97%, was obtained after the composites were sintered at various conditions. With the increase of the reinforcement content in the matrix, the composite grain showed a reduced size and equiaxed morphology, but the microstructure contained a higher amount of porosity. On the other hand, the sintering conditions did not significantly affect the microstructure.

At lower sintering temperatures, for example 800°C for 1 h, a slight reaction between Ti and BNNT was observed in a few places of the fracture surface. When the composites were sintered at 1000°C for 3 h, a majority of the BNNTs were transformed to TiB phase via reaction; no BNNTs could be observed in the matrix after sintering at 1100°C and 1200°C for 3 h. The highest room temperature compressive strength was obtained from Ti-4vol%BNNT composites, but Ti-5vol%BNNT composite showed the highest compressive strength at 500°C, irrespective of sintering conditions. Ti-4vol%BNNT composite sintered at 800°C for 1 h demonstrated a room temperature compressive strength of 985 MPa which was contributed by the nanotubes. In contrast, the highest compressive strength of 1421 MPa was obtained for the same composition when composites are sintered at 1100°C, which was contributed by the TiB phase in the matrix. In the case of high temperature (500°C) compressive strength, Ti-5vol%BNNT composite sintered at 800°C for 1 h showed the maximum compressive strength of 277 MPa. The highest compressive strength of 425 MPa was obtained for the same composition when sintered at 1200°C for 3 h. The in-situ formed reaction phases in the composite were analysed systematically by TEM imaging and EDX mapping. Composites sintered at high temperatures showed randomly oriented TiB whiskers in the matrix. A high concentration of N solid solution was identified in the Ti matrix at the regions adjacent to the nanotubes, indicating the release of N atoms from the BNNTs to diffuse towards Ti.
The formation mechanism of TiB phase in the composite was further investigated by investigating the heat treatments on Ti coated BNNT nanocomposites prepared by the sputtering process. The onset condition for the nucleation of the reaction phases between Ti and BNNT and their growth mechanism was studied by SEM and HRTEM. It was found that the nanocomposites were stable up to 700°C without any formation of the reaction phases on the surface of the nanotubes. However, when the nanocomposites were heated at 800°C for 30 min, the reaction phase nucleates on the outer surface of the nanotubes. The calculation of the lattice spacing from HRTEM identifies the phase as TiB₂. TiB₂ has its \{0001\} plane parallel to the nanotube surface, which is the largest and slowest growing face of TiB₂ crystals. A longer exposure time, up to 1 h at the same temperature, demonstrated that the nucleated phase grows into a plate-like structure which gradually consumes up the outer layers of nanotubes. The formation of TiB₂ crystals at Ti-BNNT interface improves the interfacial bonding between Ti matrix and BNNT reinforcement. At temperatures higher than 800°C, most of the TiB₂ phase transforms into TiB phase, provided that Ti atoms from the surroundings could diffuse towards it. Finally, TiB whisker forms in the composite if there is sufficient Ti available, otherwise the particle remains the plate-like TiB₂ morphology. The in-situ formed TiB whiskers distributed within the matrix act as reinforcement in the composites.

8.1 Suggestions for Future Works

Based on the outcome of this research for preparation and property development of Ti matrix composites, a number of limitations were identified which could be addressed for possible improvements in the future.

i. In the case of large quantity and high density synthesis of BNNTs, the largest quantity of nanotubes was obtained when the ball milled powder was annealed in suspended condition by the gas flow. But this consumes a lot of gas even at 1 h annealing period. The gas consumption can be significantly reduced by fitting a nozzle at the tip of gas flowing alumina tube. The high velocity of gas through the tube would effectively suspend ball milled powders inside the furnace. This condition can be further improved by reducing the furnace tube since the gas velocity is less effective in larger diameters tube. Such modification would also help to eliminate agglomerated form of the synthesized nanotubes caused by the rolling effect inside the furnace tube.

ii. The initial size of the Ti powder used in this research for preparation of the composites is too large. The Ti particles are also highly irregular and contain
lots of pores. This affected the distribution of BNNTs and h-BN within Ti powder, especially in the case of Ti-BNNT powder mixtures, nanotubes in clustered form tried to fill the pores within Ti powders. A smaller Ti powder size with spherical shape would eliminate this obstacle effectively. Spherical shape powders exhibit better packing density than the irregular shaped powders. A smaller Ti powder size would refine the grain sizes further increasing the mechanical properties. To achieve this, one approach could be ball milling of these Ti powders under Ar+5%H₂ gas atmosphere. However, the ball milling conditions would have to be optimized in order to obtain spherical shaped smaller Ti powders. Another approach could be the use of TiH₂ powder for preparation of composites. Ball milling of TiH₂ powders will not pose any risk of oxidation of powders. Also, TiH₂ powders are cheaper, easier to press due to their brittle nature and requires less pressure in obtaining green compacts.

iii. The reinforcing BNNTs and BN particles reacted with Ti at a sintering temperature above 800°C with greater than 1 h holding time. This is common for Ti composites. Similar behaviour was also observed in case of CNT, SiC, SiO₂ and other kinds of reinforcements when composites were even processed using spark plasma sintering or hot pressing process for a short duration. Therefore, the reaction between Ti and BNNT could be greatly minimized if the composites can be prepared using spark plasma sintering process. The high oxidation resistance of BNNT in this case would be advantageous. Besides, the high temperature stability of BNNT has been demonstrated, as few was observed in the fractures surfaces of the composite after sintering at 1000°C for 3 h. Another approach could be the high pressure torsion method in order to fabricate the composite which involves low temperature and high pressure. BNNTs are able to withstand the high pressure that was used in this research for the preparation of green compacts, indicating their compatibility to the high pressure torsion method.
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170


178


