

Boron Nitride Nanotubes Reinforced Metal Matrix Nanocomposites: A Review

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Abstract

Multiwalled Boron Nitride Nanotubes (BNNTs) reinforced Metal Matrix Nanocomposites (MMNCs) are discussed in this work. It is noticed that the reaction of BNNTs with Aluminum (Al) to form a compound at the interface depends on the processing condition. The processing methods include sintering, solidification, rolling, High-Pressure Torsion (HPT) and heat treatment have influenced the microstructure and mechanical properties of BNNTs filled MMNCs. The review suggests that BNNTs filled MMNCs have the potential to be used in various applications.

Keywords: High Pressure Torsion, Metal Matrix Nanocomposites, Multiwalled Boron Nitride Nanotubes, Rolling, Spark Plasma Sintering.

1.0 Introduction

Multiwalled BNNTs are under investigation as a substitute for Multiwalled Carbon Nanotubes (MWNTs) for reinforcing fillers in MMNCs¹⁻⁴. The BNNTs is emerged popular due to high inertness at the high temperature processing of metals like Al, Magnesium, etc. The BNNTs can be used as reinforcing filler for MMNCs coating

which is done using plasma atmosphere which required high inertness in harsh conditions. The BNNTs was a suitable candidate for ceramics matrix nanocomposites too. In this review, a brief about the synthesis of BNNTs is discussed. The major emphasis of this review is on the experimental investigation of BNNTs filled MMNCs. The interface aspects along with the processing of BNNTs filled MMNCs are discussed.

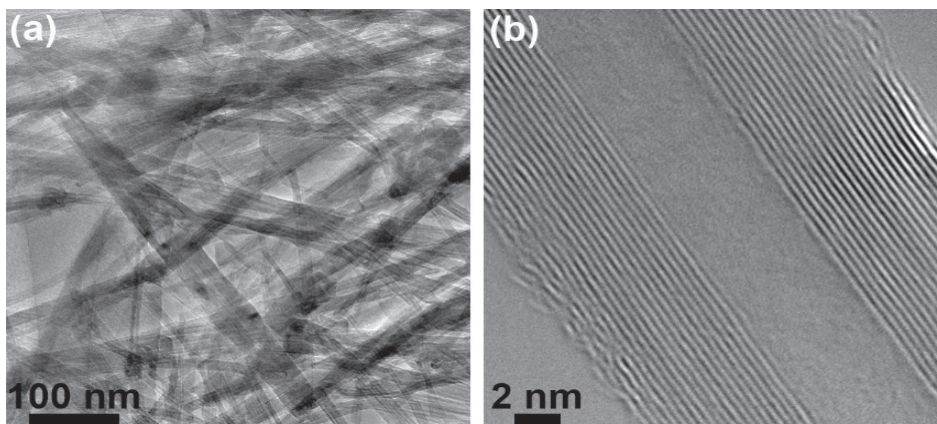


Figure 1. (a, b) TEM images of BNNTs (Reproduced with permission¹⁰).

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2.0 BNNTs Synthesis

The BNNTs are synthesized using various methods are as follows: (a) Arc discharge method (b) Chemical Vapour Deposition (CVD) method (c) Laser ablation method (d) Ball milling method⁵⁻⁹. In the case of the arc discharge method, the preferred boron nitride rod contains a chemical compound to improve the conductivity of the anode and acts as a catalyst to produce BNNTs. While in the case of the CVD method the precursor materials were used in presence of a catalyst to produce the BNNTs, and have control over the yield. The BNNTs obtained using the CVD methods are shown in Figure 1 showing the multilayers of boron nitride¹⁰. The laser ablation method was used to synthesize one or few-layers boron nitride nanotubes. Ball milling is preferred when the yield requirement is more in which the boron powder, catalyst, and nitrogen precursor were used.

3.0 Theoretical Studies on BNNTs Filled MMNCs

The theoretical studies over the BNNTs filled MMNCs were carried out by two research groups. Rezaei *et al.*¹¹ studied

the mechanical behaviour of BNNTs filled aluminum MMNCs using molecular dynamics simulation. The deformation mechanism of pure aluminum is associated with the deformation due to dislocation and the shear plane. Along the slipping plane, the atomic bonds were broken and finally, the metallic specimens fail. The BNNTs reinforced aluminum nanocomposites restrict the dislocation path which increase the strength. In addition, it was noted that the BNNTs breaks and slide inside the aluminum matrix. Rohman *et al.*,¹² investigated the interaction of BNNTs with aluminum using quantum chemical calculations. They have taken neat BNNTs and BNNTs with vacancy defects of boron and nitrogen atoms interaction with Al_4 cluster and Al surface. There exists a more distorted of Al near the vacancy sites exhibiting the reinforcing efficiency of BNNTs with vacancy defects.

4.0 Experimental Studies on BNNTs Filled MMNCs

4.1 Interface Reaction between BNNTs and Metals

The interface reaction between the BNNTs and metal is

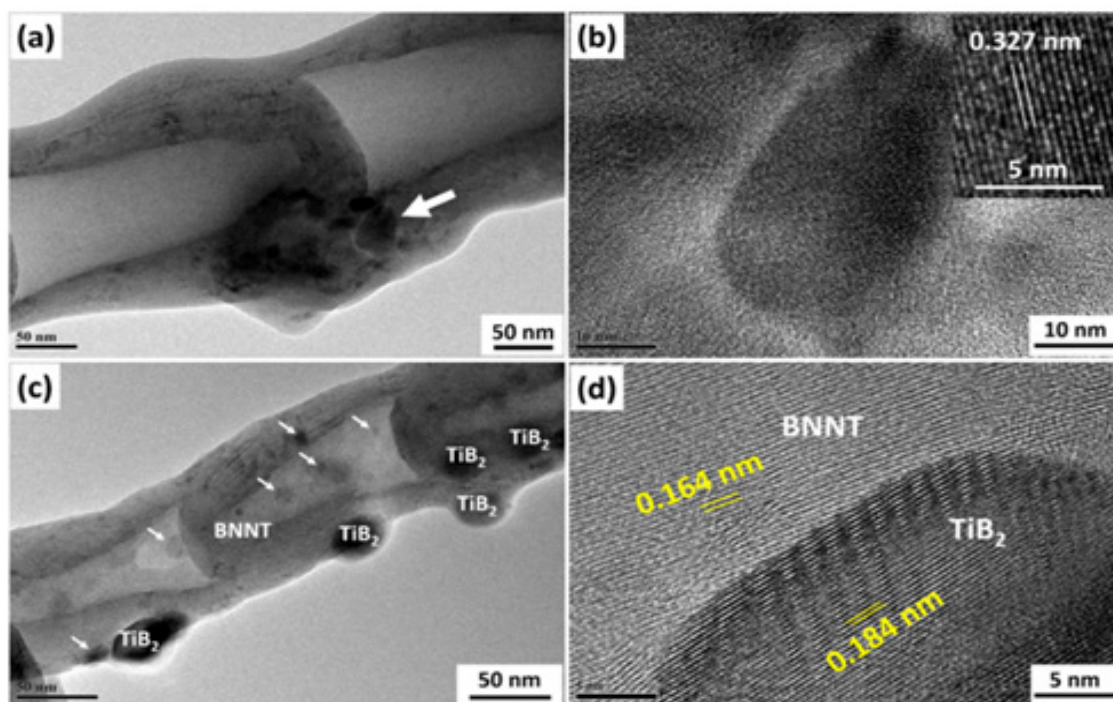


Figure 2. (a-d) TEM image of BNNTs coated with titanium (Reproduced with permission¹).

important to tailor the mechanical properties of MMCs. Mahedi *et al.*¹ coated the BNNTs with titanium through a sputtering method followed by heat treatment. Figure 2 reveals the TEM image of titanium coated BNNTs. It exhibits dark color TiB_2 formed over the surface of the BNNTs. It appears from Figure 2c that the TiB_2 nucleate and grow in size at the selective location due to heat treatment. The magnified image of Figure 2c shown in Figure 2d shows the d-spacing of BNNTs and TiB_2 . In addition, most of the nucleated TiB_2 remain in the nucleated stage. When the heat treatment temperature was increased to 1000°C for 1 hour, there was a formation of needle-shaped TiB and plate-like TiB_2 .

Lahiri *et al.*,² established experimentally the reaction between the Al and BNNTs. The experiments were carried out by mixing the BNNTs and Al powder with

the wet-mixing method followed by heat treatment near the melting temperature of 650°C for different intervals of time. With an exposure of a sufficient amount of time, the formation of AlB_2 and AlN peaks appeared with more intensity in XRD peaks. HRTEM also confirms the reaction product formation. AlN formed as spherical crystals at the interface with smaller sizes, while the AlB_2 forms as elongated crystals with comparatively large sizes. The formation of Al compound interfacial layer depends on the reactions conditions. At a higher reaction time, the interface layer formation is thicker.

4.2 Solidification of BNNTs and Metals

Nautiyal *et al.*⁴ studied the nanocomposite coating of BNNTs and Al using the plasma spray method for non-

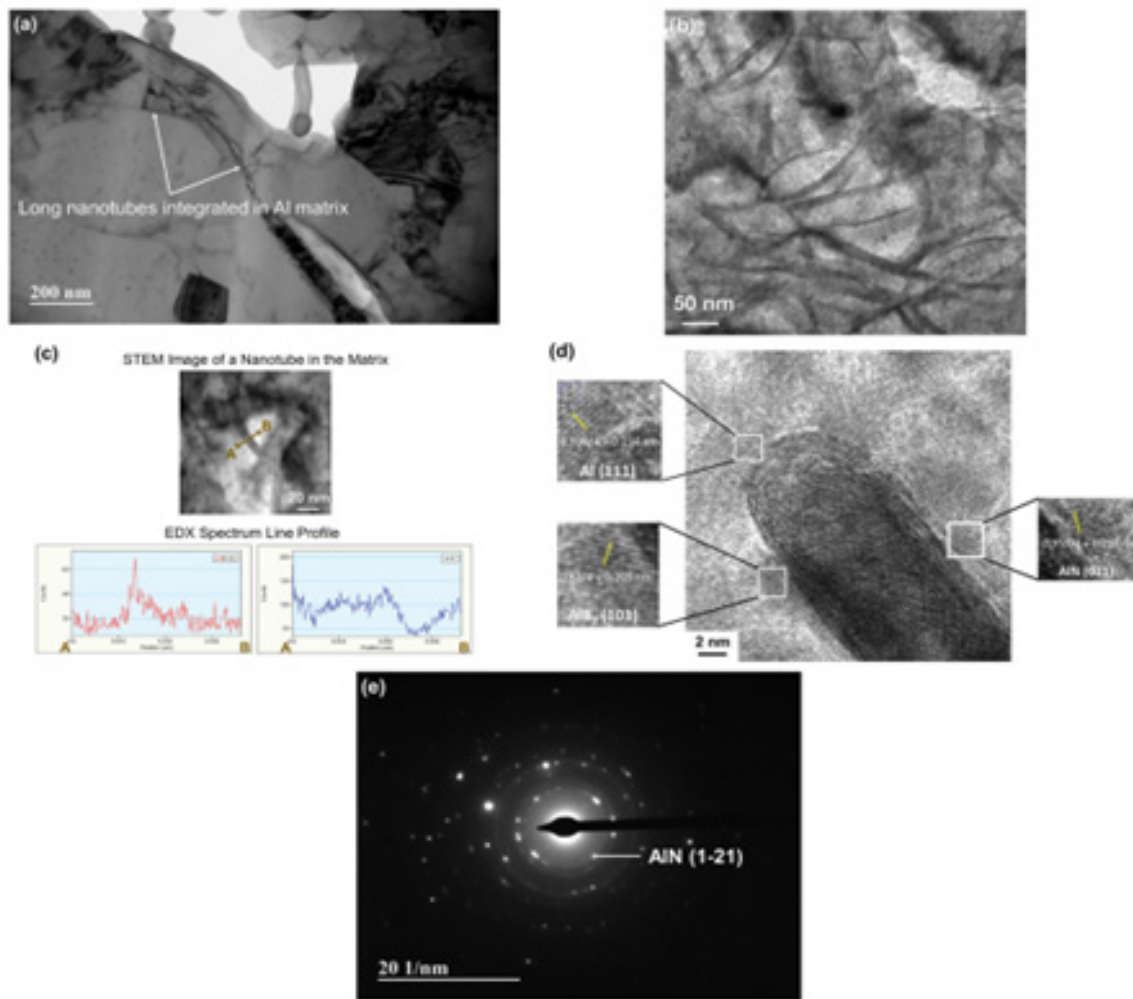


Figure 3. (a-d) TEM, (c) EDAX and (e) SAED pattern of BNNTs/Al nanocomposites (Reproduced with permission⁴).

equilibrium solidification of nanocomposite coating. Initially, they mixed the BNNTs and Al powder using surfactant through the wet chemical method. The obtained powdered was plasma sprayed over the Al substrate. Over the sprayed powdered, TEM studies were carried out. TEM studies of plasma sprayed BNNTs/Al nanocomposites coating is shown in Figure 3. Figure 3a shows the BNNTs is dispersed into the Al matrix. Figure 3b shows the network of BNNTs in Al matrix. EDAX analysis of a sample reveals the presence of BNNTs confirms the stability of BNNTs in the plasma environment (Figure 3c). The high magnification TEM shown in Figure 2d reveal the formation of compounds

of AlB_2 and AlN . The Selected Area Diffraction Pattern (SAED) suggests the presence of AlN compounds in the spray coated BNNTs/Al nanocomposites.

Nautiyal *et al.*,³ studied the equilibrium solidification of BNNTs/Al nanocomposites with a specific emphasis on reactive wetting. The Al and BNNTs of long length were premixed properly and melted in a crucible at above the melting temperature. Thereafter the Al/BNNTs melt was cooled slowly in a muffle furnace at the controlled cooling for 10 hours. Figure 4 depicts the SEM and TEM images of the BNNTs/Al nanocomposites. The SEM image shows the network of BNNTs in the Al matrix (Figure 4a). While the TEM image shows the dispersion of long-length

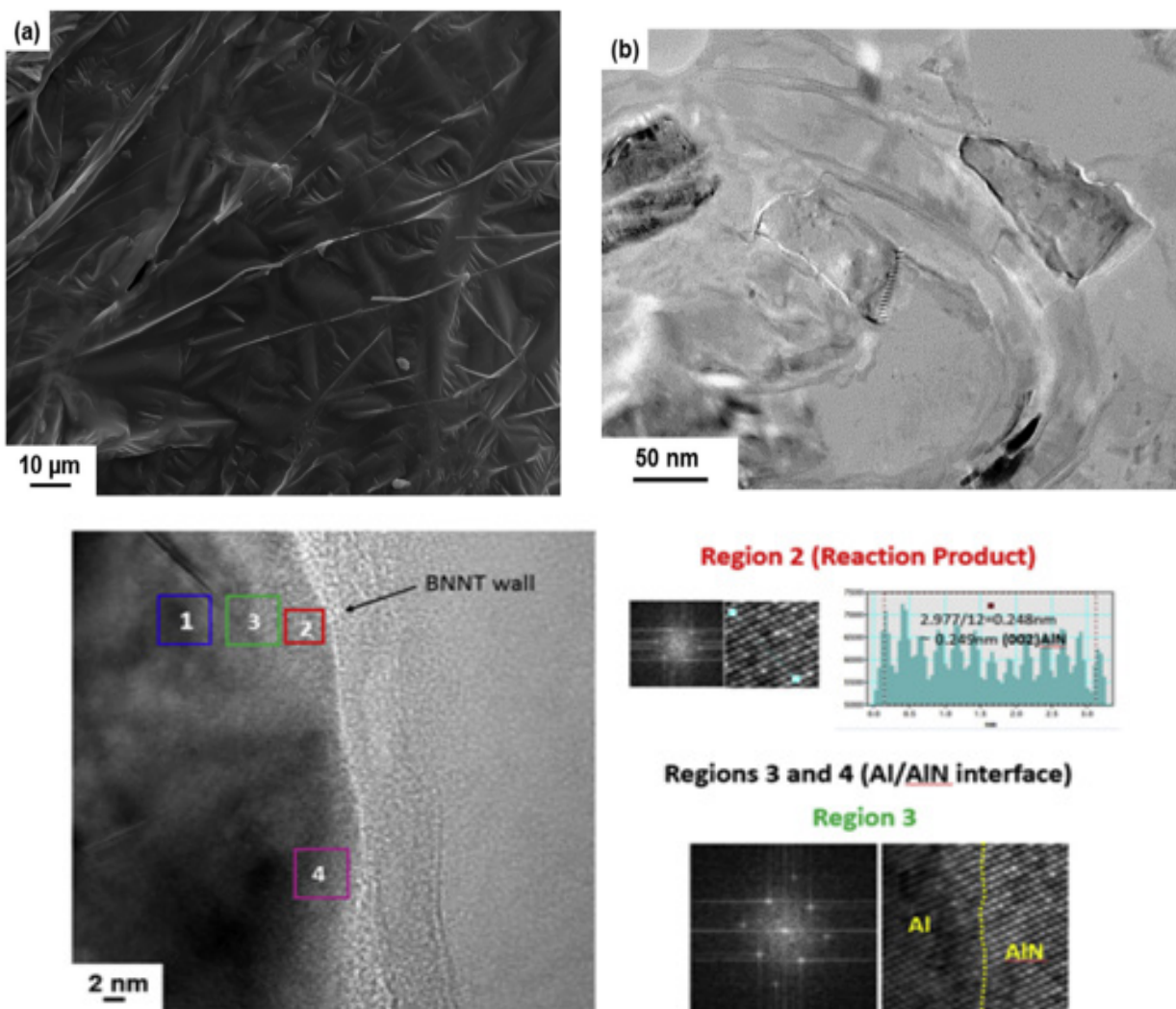


Figure 4. (a) SEM (b, c) TEM of BNNTs/Al nanocomposites (Reproduced with permission³).

BNNTs in the Al matrix (Figure 4b). At the interface of Al and BNNTs, there is a formation of the AlN compound (Figure 4c). In addition, the filling of BNNTs by molten Al was also established.

4.3 Spark Plasma Sintered of BNNTs Filled MMNCs

Spark Plasma Sintering (SPS) is one of the advanced methods for sintering of metal powder. Lahiri *et*

*al.*¹³ used the SPS method to sintered the BNNTs/Al nanocomposites. The volumetric concentration of BNNTs in Al matrix were 0.2-5 vol.% and consolidated in disk of 20 mm diameter and 5 mm thickness. XRD of BNNTs/Al nanocomposites do not show the formation of reaction product between Al and BNNTs. The XRD of BNNTs/Al nanocomposite shows the appearance of the basal plane peak of hBN confirming the presence of BNNTs in the Al matrix. The SEM image of Figure 5 shows the ductile fracture mechanism of both the Al and BNNTs/Al

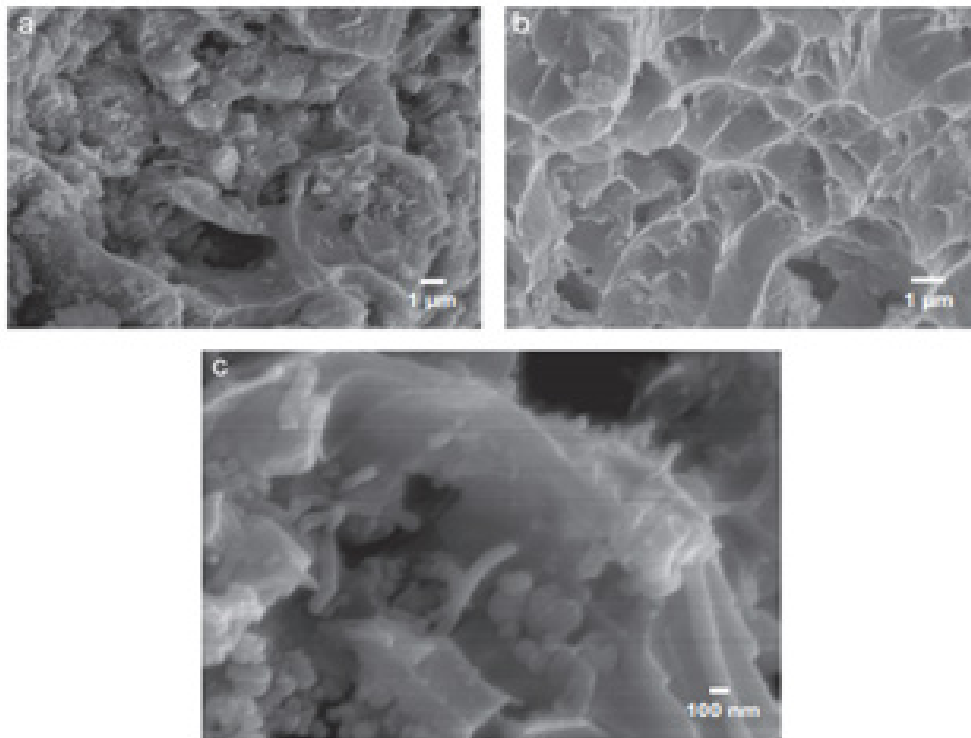


Figure 5. SEM images of (a) Al (b, c) BNNTs/Al nanocomposites (Reproduced with permission¹³).

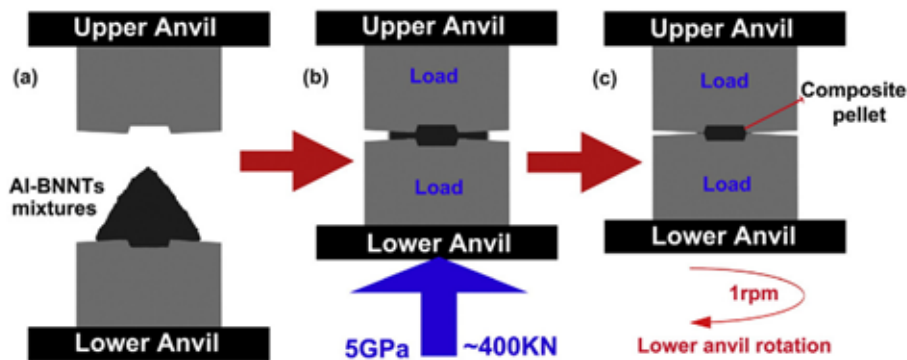


Figure 6. (a-c) Schematic of high pressure torsion processing of nanocomposites (Reproduced with permission¹⁴).

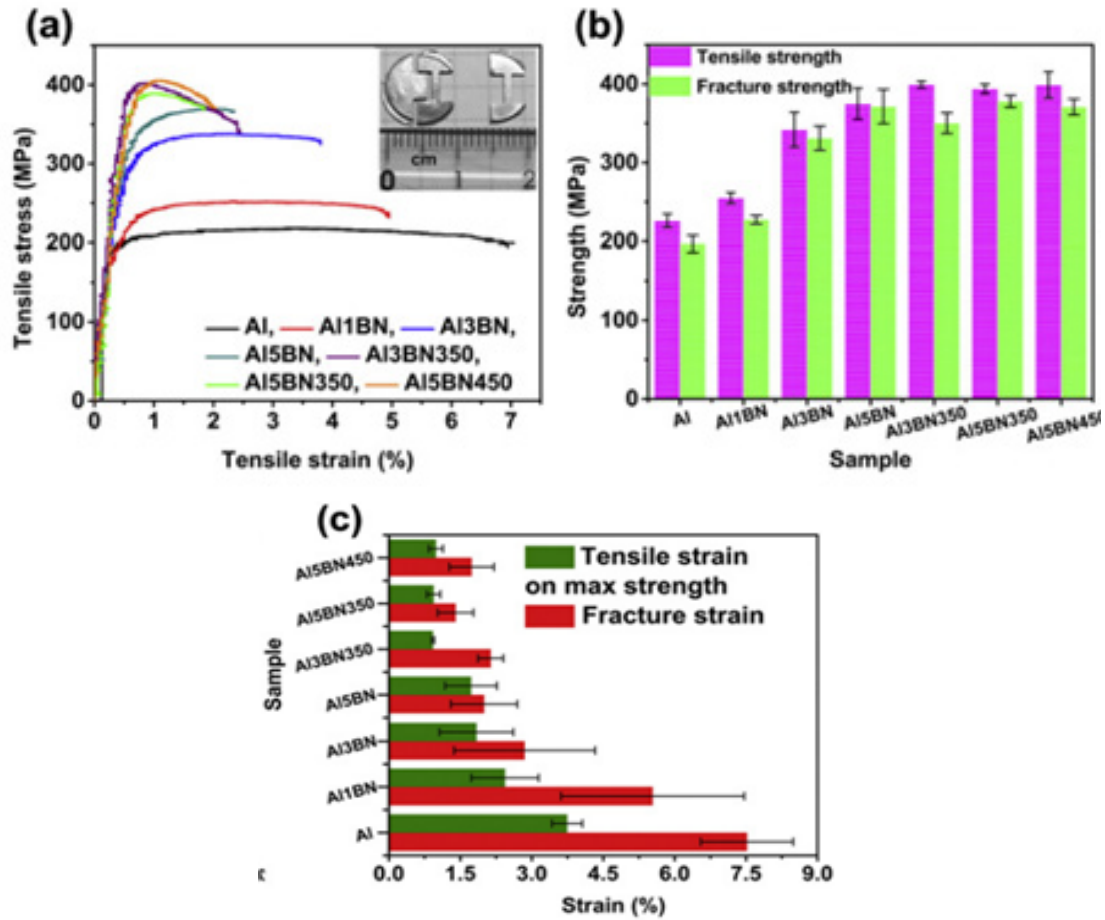


Figure 7. (a) Stress-strain curves, (b) Strength and (c) Strain of BNNTs/Al nanocomposites (Reproduced with permission¹⁴).

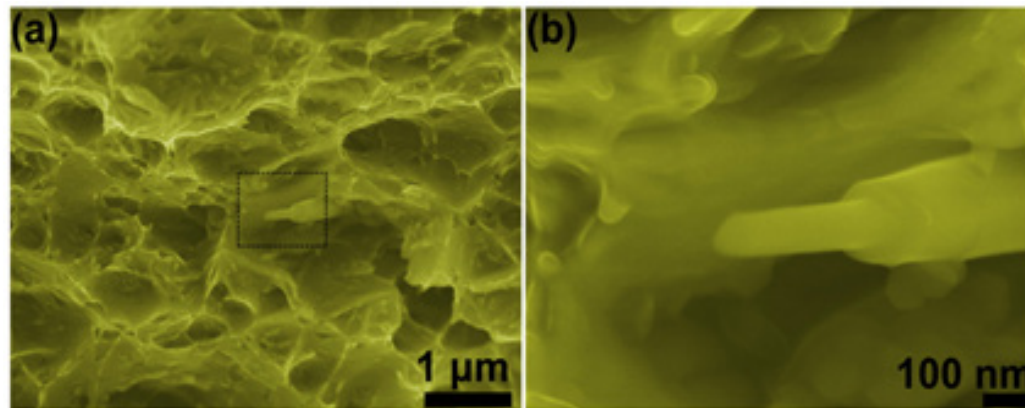


Figure 8. (a-b) SEM images of BNNTs/Al nanocomposites (Reproduced with permission¹⁴).

nanocomposite. The thin ridges on the fractured image were observed. It was due to the localized deformation of Al in presence of BNNTs. The SEM image of Figure

4c shows the pull-out BNNTs from the Al matrix. The structure of BNNTs/Al nanocomposites also reveals the dense structure from SEM and density measurements.

The obtained BNNTs/Al nanocomposites can be rolled up to 75% during cold rolling operation which signifies the importance of formability achieved in deformation operation.

4.4 High Pressure Torsion Processing of BNNTs Filled MMNCs

High Pressure Torsion (HPT) is an important method to process metal powder. The schematic of this process to process BNNTs/Al nanocomposite is shown in Figure 6¹⁴. It consists of two anvils under which the BNNTs/Al was compressed so that the applied load is 5 GPa. This load is applied for some time then the lower anvil is rotated at 1 rpm to form the product. In this process, the ultrafine grains were developed due to the severe plastic deformation because of which Al(BNO) phase forms. The Al(BNO) phase further developed due to annealing. The tensile properties results of BNNTs/Al nanocomposites are shown in Figure 7. It shows that

the neat Al has high ductility and tensile strength of 190 MPa. The dispersion of 3 wt.% of BNNTs in the Al matrix shows the maximum enhancement in tensile strength, thereafter the tensile strength enhancement is minimal with an increase in BNNTs concentration. Annealing of BNNTs/Al nanocomposites increases the tensile strength but decreased the ductility. The SEM image reveals the ductile-like fracture with pull out of BNNTs from the Al matrix (Figure 8). Yamaguchi *et al.*¹⁵ showed the HPT processing of BNNTs/Al nanocomposites exhibit the dispersion of BNNTs in grains for Al which increases the hardness significantly.

4.5 Rolling of BNNTs Filled MMNCs

Bisht *et al.*,¹⁶ processed the BNNTs/Al nanocomposites by conventional powder metallurgy route followed by the warm rolling. Figure 9 shows the optical microscope images of sintered, rolled, annealed neat Al and BNNTs/Al nanocomposites. The sintered Al shows the non-

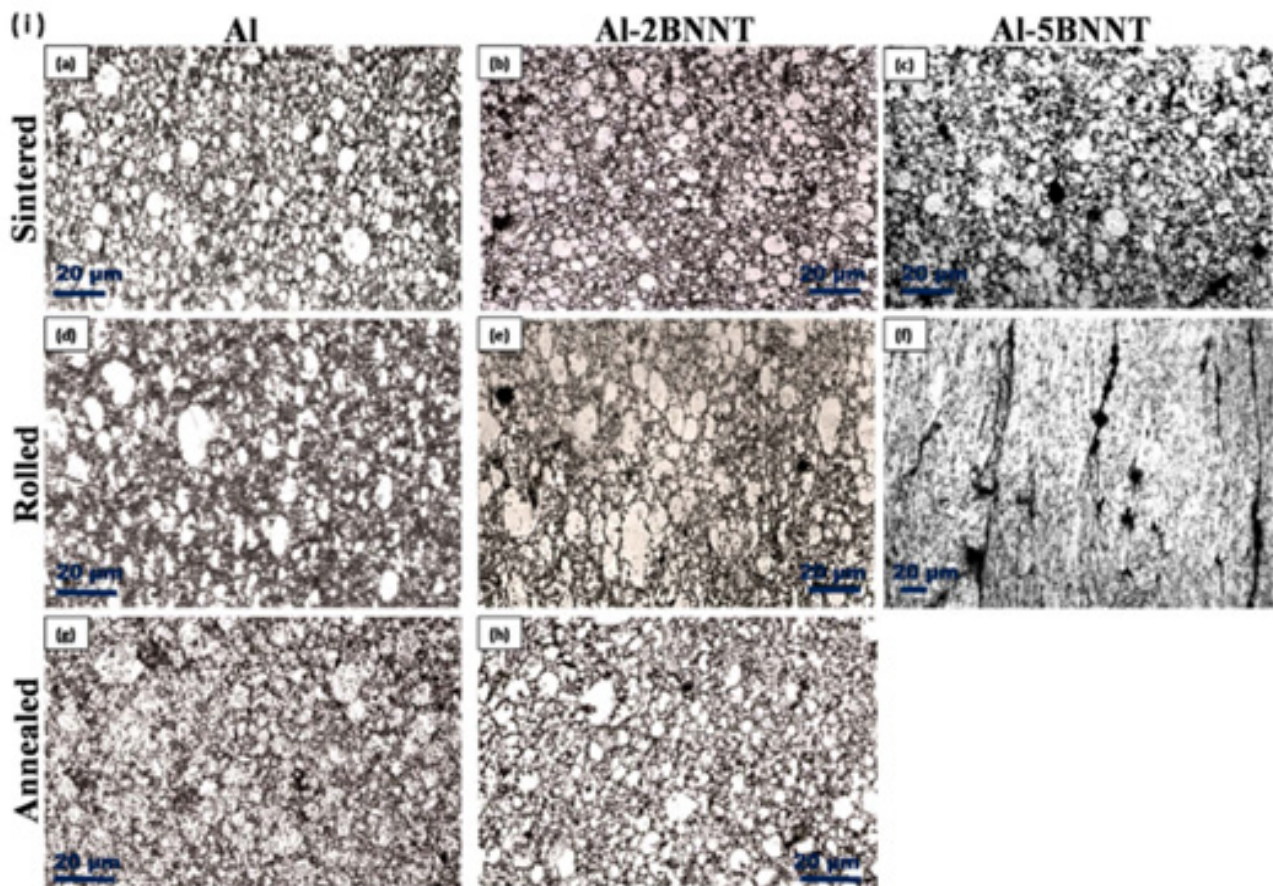


Figure 9. (a-c) Sintered, (d-f) Rolled, and (g-h) Annealed Optical microscope images of BNNTs/Al nanocomposites (Reproduced with permission¹⁶).

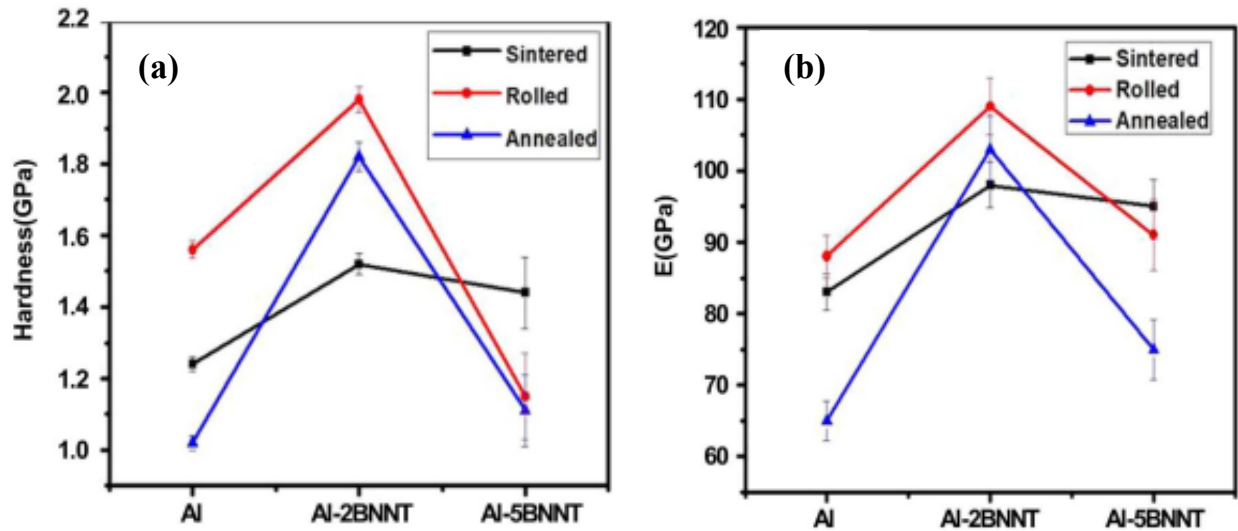


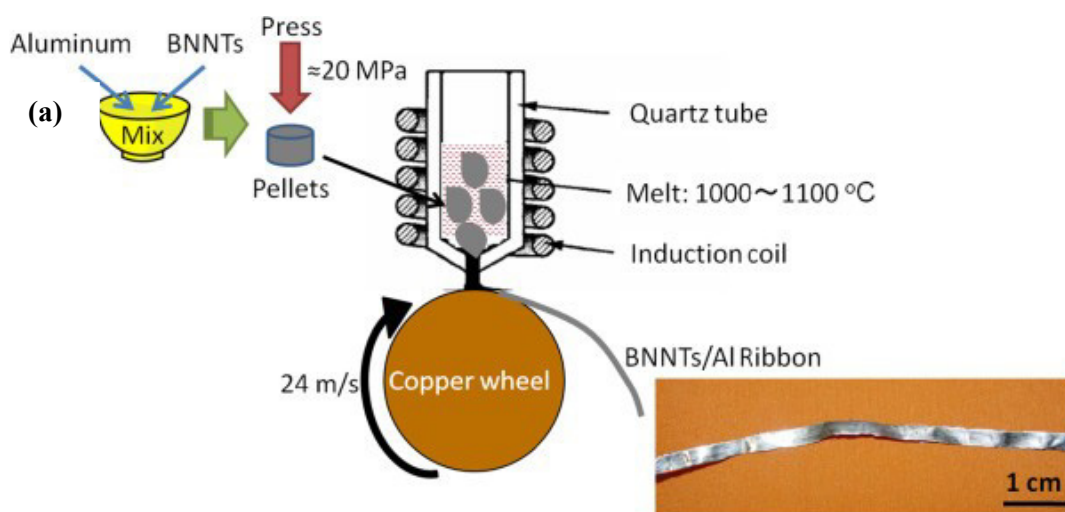
Figure 10. (a) Hardness and (b) elastic modulus of BNNTs/Al nanocomposites (Reproduced with permission¹⁶).

uniform distribution of the size of grains (Figure 9a). While the sintered BNNTs/Al nanocomposites show the uniform distribution of the size of grains of Al in presence of BNNTs due to restriction of grain growth by pinning of grain boundary (Figure 9b-c). Upon rolling, the grains of Al (Figure 9d) and BNNTs/Al nanocomposites (Figure 9e) were elongated along the rolling direction. Rolling changes the grains aspect ratio. The heat treatment of rolled Al (Figure 9d) and BNNTs/Al nanocomposites (Figure 9e) sheets shows the recrystallization of grains. The nanoindentation studies of Al and BNNTs/Al nanocomposites are shown in Figure

10. The hardness and elastic modulus of 3 wt.% BNNTs filled Al nanocomposites film is highest as compared to neat Al sheet. The recrystallized grain due to annealing has lower hardness and elastic modulus of 3 wt.% BNNTs filled Al nanocomposites as compared to rolled 3 wt.% BNNTs filled Al nanocomposites.

4.6 Melt-spun Ribbon of BNNTs Filled MMNCs

Yamaguchi *et al.*¹⁵ investigated the melt-spun BNNTs/Al nanocomposites ribbon. The schematic of melt-



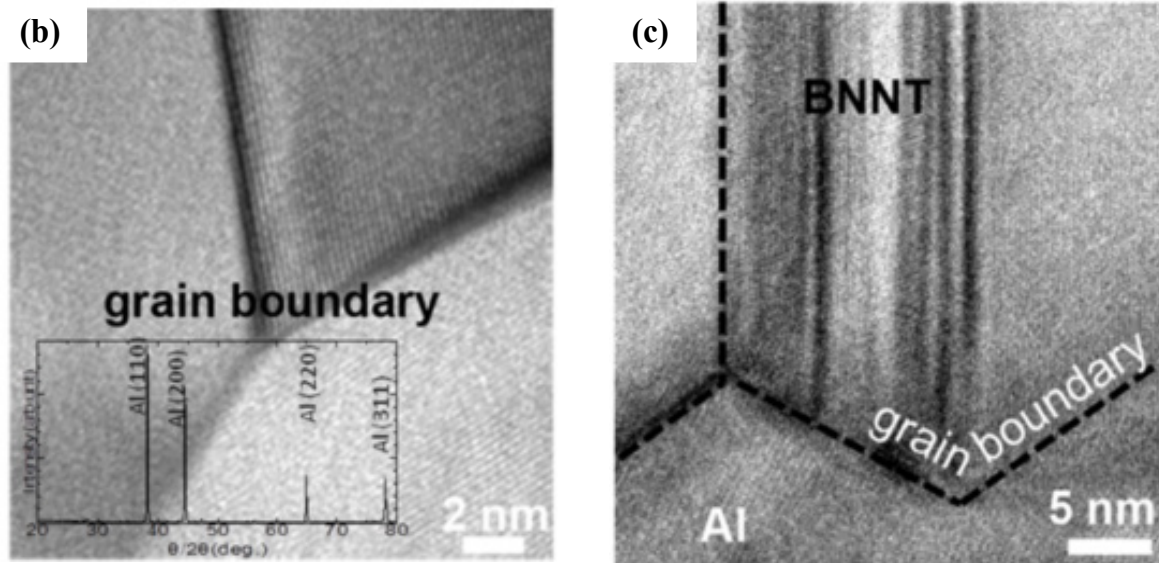


Figure 11. (a) Schematic of melt-spun setup and TEM images of (b) Al (c) of BNNTs/Al nanocomposites ribbon¹⁰.

spun setup details is shown in Figure 11a. Initially, the powdered mixture of BNNTs/Al was taken and pressed in a hydraulic press to form pallets. Then the BNNTs/Al pallets were put inside the oven over there the melting takes place. After melting, BNNTs/Al melt was rolled over the copper roll rotated at a fixed revolution. Figure 11b shows the TEM image of the Al ribbon exhibiting the grain and grain boundary. The incorporation of BNNTs in the Al matrix and melt-spun in ribbon form shows the BNNTs are localized at the interface of the grain boundary of Al (Figure 11c). The melt-spun ribbon of BNNTs/Al nanocomposites shows Young's modulus value of 35GPa as compared to the neat Al ribbon of 15 GPa.

5.0 Conclusion

The BNNTs filled MMNCs were reviewed in this paper. The synthesis method of BNNTs was briefly discussed. The interface aspect of BNNTs with metal was specifically discussed. It is noticed that the reaction of BNNTs with aluminium to form a compound at the interface depends on the processing condition. The processing methods include sintering, solidification, rolling, High Pressure Torsion (HPT) and heat treatment have influenced the microstructure and mechanical properties of BNNTs filled MMNCs. The review suggests that BNNTs filled

MMNCs have the potential to be used in various applications.

6.0 References

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