



Original Research Paper

# Making ultra-high strengthening and toughening efficiency in hybrid reinforcing of aluminum laminated composites via dispersion engineering

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## ABSTRACT

To overcome the strength-ductility trade-off dilemma, herein we propose a hybrid in-situ/ex-situ reinforced aluminum matrix composite to achieve a uniform dispersion of reinforcements and strong reinforcement-matrix interfacial bonding. To exploit the pros of inter/intra granular dispersion of reinforcements, nano- Al<sub>3</sub>BC particles have been in-situ synthesized into ultrafine-grained (UFG) Al grain interior reinforced by carbon nanotubes (CNTs) via an elemental powder mixture, mechanical activation and subsequent annealing process. The in-situ nano-scaled Al<sub>3</sub>BC were uniformly distributed inside the elongated ultrafine Al grains, enabling stronger dislocation pinning and retention, providing stronger effective stress which consequently helps to enhance strength and strain hardening. The as-fabricated (Al<sub>3</sub>BC, CNT)/UFG Al exhibits simultaneous enhancement in strength (394 MPa) and total elongation (19.7 %) compared with its counterpart without the nano-Al<sub>3</sub>BC, suggesting the promising strengthening effects of in-situ/ex-situ reinforcing benefitting from the uniform dispersion and the strong semi-coherent interface with the matrix.

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## 1. Introduction

Hybrid reinforcing is novel and significant strategy with the core idea of the hybrid reinforcements to exert their respective advantages, and to fabricate advanced metal matrix composites (MMCs) that is nowadays motivated by the purpose to overcome the strength-ductility trade-off [1–5]. Thanks to the higher efficiency of nano-sized reinforcements compared to counterpart micron-sized ones [6], a step forward has been taken in the direction of simultaneous improvement of strength and ductility. Although, the use of ex-situ reinforcement nanoreinforcement always brings the dilemma of uniform dispersion in MMCs [7,8]. Along with all the advantages of using ex-situ reinforcements, deleterious aspects such as the formation of incoherent interfaces between the reinforcement-matrix, the essence of problems such as stress concentration and deformation discontinuity at the microscale scale during the deformation process come out [9,10]. Therefore, it seems that the simultaneous use of the benefits of in-situ and ex-situ reinforcements as a hybrid reinforcing strategy would be one of the optimal ways to realize the simultaneous

improvement of strength and ductility in MMCs. The essence of having a laminated structure accompanied with hybrid reinforcing significantly contributes to hetero-deformation induced (HDI) stress strengthening and sustained strain hardening, making the key mechanical properties of GNS-Cu/Al. What's more, high-performance reinforcing and a tailored architecture has been gained in reduced graphene oxide (RGO)-CNT hybrid /Al composite prepared by a composite flake assembly process due to the formation of a planar network of RGO and CNT, which improves the load transfer efficiency between the matrix and the reinforcement in composites [5]. Recently, a strong but tough aluminum matrix composite (AMC) reinforcing with graphene oxide (GO)-CNT hybrid were prepared by powder metallurgy [4]. The strength of the composites was improved by the synergistic effect of carbon nanotubes, in-situ Al<sub>3</sub>C<sub>4</sub> and GO. Very recently, superior tensile properties of AMC reinforced by both in-situ Al<sub>2</sub>O<sub>3</sub> nanoparticles and ex-situ GNSs was developed via manipulating the PM route [11]. The composite possesses a high tensile strength of 464 MPa and appreciable amount of ductility (8.9 %), resulted from the combination effect of grain refinement, in-situ Al<sub>2</sub>O<sub>3</sub> nanoparticles and exsitu GNSs. It is inferred the presence of a synergetic strategy between in-situ and ex-situ reinforcements accompanied with a tailored architecture could provide significant contribution of both

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## Nomenclature

$\alpha_i$	The $i$ 'th parameter of the vdW interaction model, (-)	$I$	Aggregate's inertia moment, ( $\text{kg}\cdot\text{m}^2$ )
$\beta$	Stretching exponent, (-)	$k_B$	Boltzmann's constant, ( $\text{m}^2\cdot\text{kg}\cdot\text{s}^{-2}\cdot\text{K}^{-1}$ )
$\epsilon$	Lennard-Jones potential characteristic energy, ( $\text{J}/\text{mol}$ )	$k_f$	Aggregate's fractal prefactor, (-)
$\gamma$	Angle between two vectors, (-)	$m_i$	The $i$ 'th particle's mass, ( $\text{kg}$ )
$\Gamma_{12}$	Center-center distance between aggregates, ( $\text{m}$ )	$N_p$	Number of primary particles, (-)
$\nu$	Frequency of electrostatic interaction, (-)	$n_z$	Number z-planes, (-)
$\rho_i$	The $i$ 'th particle atom number density, ( $\text{m}^{-3}$ )	$n_{s,xy}$	Number spheres in xy plane, (-)
$\sigma$	Lennard-Jones potential characteristic distance, ( $\text{m}$ )	$r$	Radial distance, ( $\text{m}$ )
$\theta$	Angle between two vectors, (-)	$r_s$	Radius of a circle, ( $\text{m}$ )
$\epsilon_i$	The $i$ 'th particle dielectric constant, (-)	$R_{\max}$	Aggregate's maximum radius, ( $\text{m}$ )
$\varphi$	Aggregate's packing factor, (-)	$R_g$	Aggregate's gyration radius, ( $\text{m}$ )
$\bar{M}$	Rotation matrix, (-)	$R_i$	The $i$ 'th eigenvalue of the inertia moment matrix, (-)
$\xi$	Aggregate's large scale cut-off characteristic distance, (-)	$R_{pi}$	The $i$ 'th primary particle radius, ( $\text{m}$ )
$A_{13}$	Anisotropy coefficient, (-)	$T$	Absolute temperature, ( $\text{K}$ )
$A_{\text{Ham}}$	Hamaker's constant, ( $\text{J}$ )	$V$	Aggregate's volume, ( $\text{m}^3$ )
$C$	London dispersion coefficient, ( $\text{J}\cdot\text{m}^6$ )	$V_a$	Aggregate's total volume, ( $\text{m}^3$ )
$d$	Center-center distance, ( $\text{m}$ )	$V_i$	The $i$ 'th particle volume, ( $\text{m}^3$ )
$D_f$	Aggregate's fractal dimension, (-)	$V_p$	Primary particle volume, ( $\text{m}^3$ )
$D_v$	Volume-equivalent diameter, ( $\text{m}$ )	$W$	Interaction energy, ( $\text{J}$ )
$F$	Interaction force, ( $\text{N}$ )		
$g$	Radial distribution function, (-)		
$h$	Planck's constant, ( $\text{m}^2\cdot\text{kg}\cdot\text{s}^{-1}$ )		

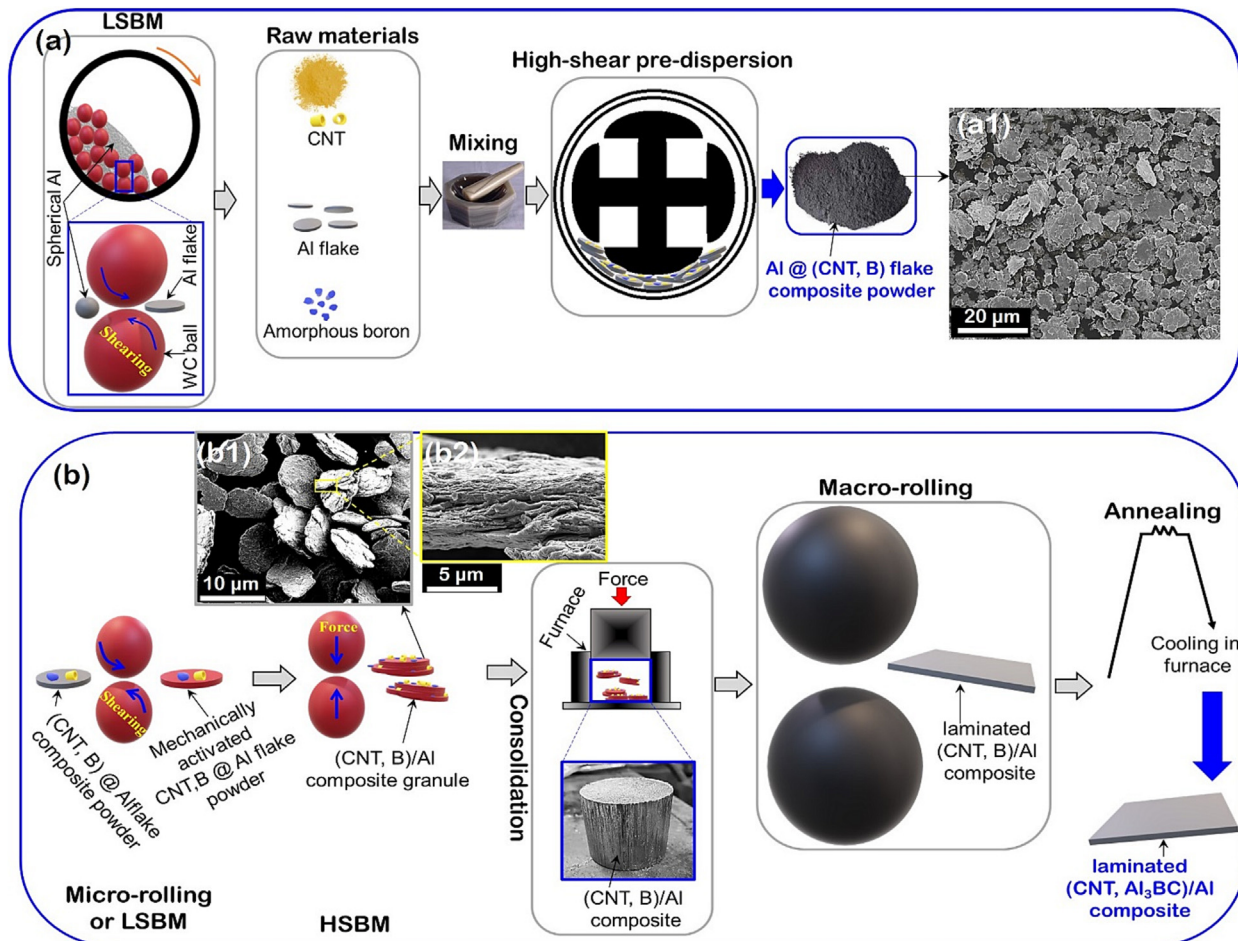
strengthening and toughening mechanisms to achieve the best combination of strength-ductility. Promisingly, the configuration of microstructure in mesoscale and uniform spatial distribution of hybrid reinforcements offer additional potential in tuning the mechanical properties of advanced AMCs [12]. Motivated by the above considerations, an easy and innovative route on basis of elemental powder strategy to in-situ-synthesize was employed to introduce nano- $\text{Al}_3\text{BC}$  into AMCs reinforced with CNT to attain a significant synergy of high strength and toughness. In the present work, a smart and efficient way of powder metallurgy (PM) (referred to as flake PM in the literature [1,13–16]) was developed by combining high-speed predispersion and dual-speed ball milling (low speed ball milling (LSBM) & high speed ball milling (HSBM)) to produce (CNT,  $\text{Al}_3\text{BC}$ )/Al composites, in which the CNTs were first mechanically deagglomerated and uniformly coated onto the surface of the flake Al powder via the dry particle coating mechanism in a fast and uniform dispersion and better protection for the CNTs from subsequent damage. The formation of a composite between the reinforcing phase and the matrix involves a series of steps, including material selection, powder preparation, dispersion, mechanical milling, and subsequent annealing. In this innovative process, the  $\text{Al}_3\text{BC}$  nanoparticles were synthesized in-situ after the final processing step, the annealing process. Each step is critical to obtain a well-dispersed, homogeneous composite material with tailored properties, as your study shows. Accordingly, the combination of plastic deformation, strain hardening, and fragmentation ultimately leads to the formation of the composite. The reinforcing elements, such as  $\text{Al}_3\text{BC}$  and CNTs, are integrated into the Al matrix, resulting in a composite material with a microstructure that improves the specific properties.

## 2. Experimental

The fabrication of (1 wt%  $\text{Al}_3\text{BC}$ , CNT 0.45 wt%)/Al composites include the high-speed shearing process for breaking CNTs clusters and B agglomerations uniformly coating on the surface of the Al flakes (Fig. 1a) and the micro-micro rolling (MMR) process (Fig. 1b) [17,18] for producing the laminated composites. Details

of the experimental are given in the following. The atomized spherical pure Al powders (6  $\mu\text{m}$ ), amorphous boron, and the pristine MWCNTs (1.5 wt%, diameter: 30–50 nm, length: 0.3–0.5  $\mu\text{m}$ ), synthesized by means of chemical vapor deposition (CVD), were used as raw materials. Generally, CVD-grown CNTs have a few defects and significant amorphous carbon coating on the tube surface [19], which promote the formation of an  $\text{Al}_3\text{C}_4$  and  $\text{Al}_3\text{BC}$ . The spherical Al powders is firstly ball milled at 120 rpm for 15 h to obtain the Al flakes with thickness about 300 nm (as shown in Fig. 1(a)). To accommodate a uniformly coated CNTs and B particles on the Al flakes, CNTs, Al flakes and B particles were firstly mixed in molar ratio of  $\text{Al}/\text{B}/\text{CNT} = 3/1/1$  in an agate mortar, then high-shear pre-dispersion processed (at 1500 rpm, 30 min). The prepared flaky-shaped powders and 2 wt% stearic acid with a ball-to-powder ratio 20:1 was then treated by LSBM (LSBM: 10 h, 120 rpm) to mechanically activated nanocomposite building blocks (CNT, B @ Al flakes), followed by HSBM (HSBM: 0.5 h, 300 rpm) to fabricate Al@ (CNT, B) composite powder. In order to avoid self-ignition, the ground powders were taken out of the jar after the temperature (T) dropped to around room T (26°C). After degassing at 400 °C, the composites powders were compacted, vacuum sintered (600°C, 2 h) and extruded (420 °C, ratio of 25:1). Then to further consolidate the composite, the plate was firstly cold rolled (reduction of 50 %) at room T and subsequent annealing (at 800°C, 3 h, flowing argon) to synthesize in-situ  $\text{Al}_3\text{BC}$ . The final main composite contained 1 wt%  $\text{Al}_3\text{BC}$ , 0.45 wt% CNTs, 0.1 wt%  $\text{Al}_3\text{C}_4$ , and 2.6 wt%.  $\text{Al}_2\text{O}_3$ . For comparison, the 1.5 wt% CNT/Al without B addition was also fabricated with the same procedure.

Microstructural analyses were carried out using high-resolution transmission electron microscopy (HR-TEM, Talos F200X G2), scanning transmission electron microscopy (STEM), and electron backscattered diffraction (EBSD, NordlysMax3, Oxford, SEM equipped with EDAX Velocity Super EBSD detector with a length step of 40 nm). Grain diameters were estimated by measuring the length and width at least 350 grains in EBSD images. The Raman spectroscopy using the 532 nm line of an  $\text{Ar}^+$  laser as the excitation source and an electrochemical dissolution method [20] were used to evaluate the structural integrity of CNTs and the reaction between CNTs and Al. XRD analyses were performed using a



**Fig. 1.** Schematic diagram of (a) preparation of flakey-shape (CNT,B)@Al composite powder (a1: SEM image of flakey-shaped Al particles), and (b) fabrication laminated (CNT, Al<sub>3</sub>BC)/Al composites via micro-macro-rolling (MMR) process (b1,b2: SEM images of (b1) cold welded, and (b1)nanolaminated structure of each Al particles).

Rigaku D/Max-2500 X-ray diffractometer with Cu K $\alpha$  ( $\lambda = 0.15406$  nm) radiation. The dislocation density of samples was analyzed using [21]

$$\rho = (3\sqrt{2}\pi\langle\epsilon^2\rangle^{1/2})/(Db)$$

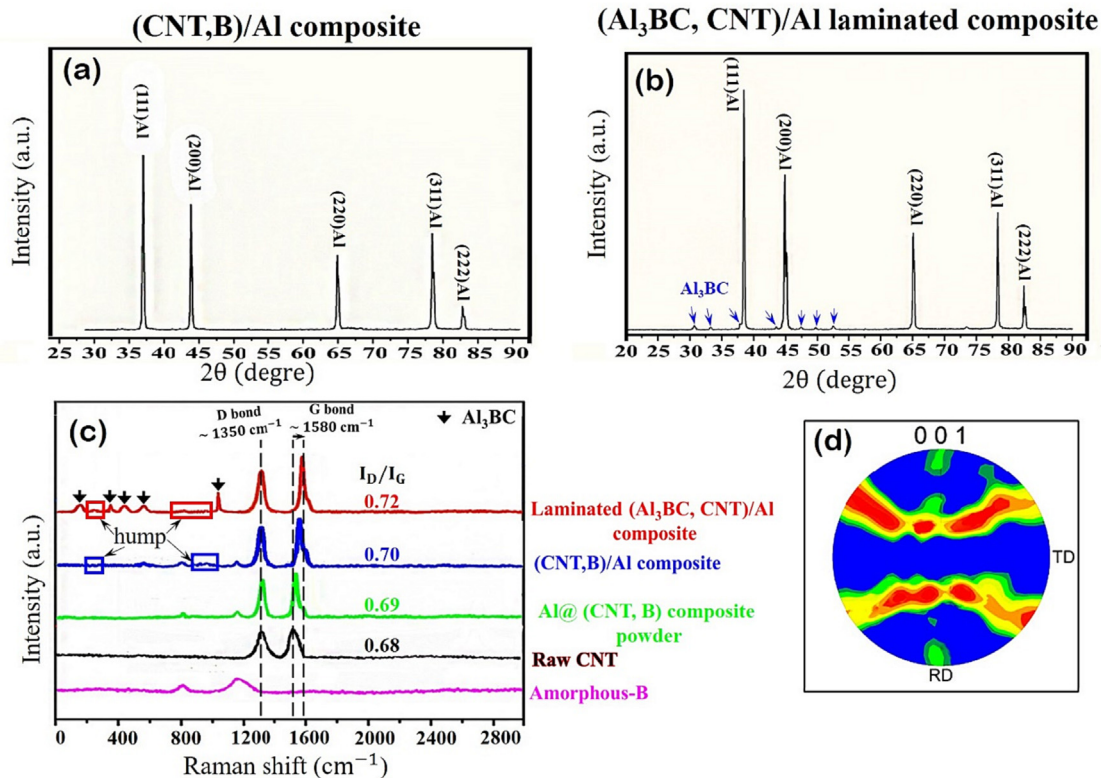
Where  $D$  is the equivalent average grain size,  $\langle\epsilon^2\rangle^{1/2}$  is the micro strain,  $\rho$  is the dislocation density,  $b$  is Burgers vector of Al, which is 0.286 nm [22]. The as-fabricated composite was sectioned into tensile specimens along the rolling direction (RD), and tensile tests were carried out at a constant strain rate of  $1 \times 10^{-4} \text{ s}^{-1}$  at room T.

### 3. Result and discussion

To obtain composite material fragments from raw powder through mechanical ball milling, several fundamental material science phenomena come into play. The powder deformation mechanism is dominated by the force, frequency of ball-to-powder collision and milling time [23,24]. Mechanical ball milling induces high-energy collisions between milling balls and powder particles, leading to plastic deformation (forming flakey shaped-powder particles especially in light alloys powders), work hardening, and fragmentation. Plastic deformation involves the permanent reshaping of materials without fracture, while work hardening increases material strength and hardness due to the

accumulation of dislocations. In a planetary ball mill, there are two forces at play when things collide: one compressing force, and the other shearing force. The compressing force from balls impacting directly mostly makes the powder flattening, cold-welding, or even at larger rotational speed, and longer milling time, breaking into pieces. On the other hand, the shear force, which happens when balls impact from the side, rotate, or friction of balls, helps disperse nano particles evenly. All these processes are crucial for achieving a well-dispersed composite material with tailored properties. Moreover, subsequent annealing, if applied, further promotes bonding and consolidation. The present study the smart and efficient route adopted is used these scientific principles to create composite materials with improved characteristics.

Diffraction peaks of Al<sub>3</sub>BC and Al were detected in (Al<sub>3</sub>BC,CNT)/Al composite (Fig. 2b), while only Al peaks were found in (B,CNT)/Al composite (Fig. 2a). The formation of Al<sub>3</sub>BC is mostly caused by the reaction Al particles with the B element and the carbon formed due to the decomposition of stearic acid during fabrication process, and subsequent annealing [25]. Indeed, due to the appearance of some area where boron and carbon atoms are supersaturated, Al<sub>3</sub>BC particles are in-situ nucleated as homogeneously in solid state with a limited growth rate. In fact, due to very low solubility of boron and carbon atoms in Al especially at solid state reactions [26,27], the growth process of Al<sub>3</sub>BC particles is soon compromised by the deficiency of carbon and boron atoms, consequently nanoscale Al<sub>3</sub>BC particle are formed. However, the presence of Al<sub>3</sub>C<sub>4</sub>



**Fig. 2.** (a,b)XRD spectra, and (c)Raman spectra of the understudy materials; (d) (001) pole figure of a typical (Al<sub>3</sub>BC,CNT)/Al laminated composite. (All the tested sample plane perpendicular to the RD).

effectively contribute to heterogeneously nucleate platelet Al<sub>3</sub>BC particles with submicron size [28,29]. In this concept, It should be noted that the characteristic peaks of Al<sub>3</sub>C<sub>4</sub> phase have not been observed in Al@(CNT,B) composite powder due to either very low relative content or the lack of formation. In addition, no specific peak of Al<sub>3</sub>C<sub>4</sub> detected neither in the (CNT,B)/Al composite nor in the (Al<sub>3</sub>BC,CNT)/Al laminated composite. This is more likely due to either no reaction between broken CNTs, or low relative content. Comparing the peaks intensity, one can be found that the ratio of {111} intensity to {200} increased after MMR process, developing a strong <111> fiber texture, verified by a typical (001) pole figure shown in Fig. 2d.

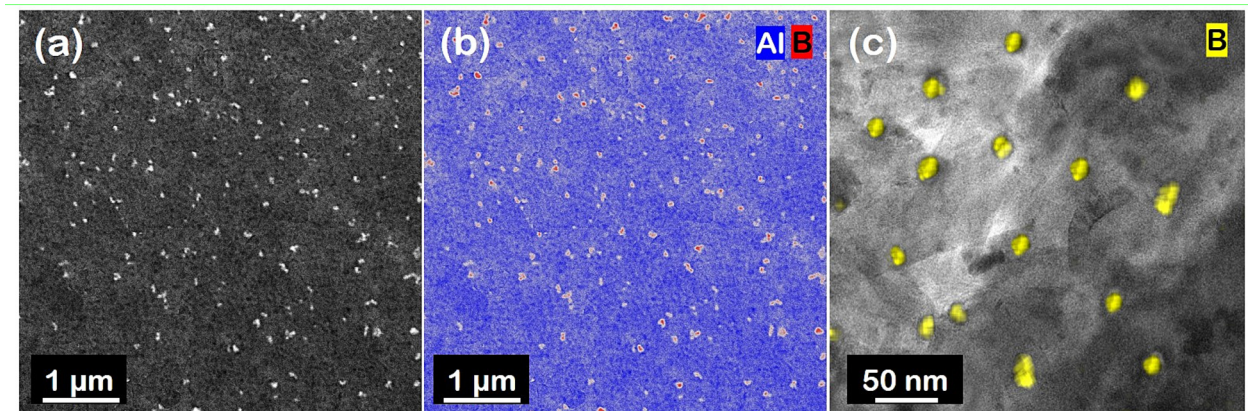
As shown in Fig. 2c, the relative intensity ratio of I<sub>D</sub>/I<sub>G</sub> of (Al<sub>3</sub>BC, CNT)/Al composite increased to 0.72 while were 0.7, 0.69 and 0.68 for (CNT,B)/Al composite, Al@(CNT,B) composite powder and raw CNTs, which implies that there was almost no serious damage to CNTs during pre-dispersion, extrusion and MMR processes. In addition, only a peak shift of G-band from 1580 cm<sup>-1</sup> to 1594 cm<sup>-1</sup> was semi-quantitatively detected in the (Al<sub>3</sub>BC, CNT)/Al composite, indicating might be originated from the infiltration of Al atoms in CNTs, causing slight distortion of sp<sup>2</sup> bonding structure of CNTs. The characteristic peaks of Al<sub>3</sub>C<sub>4</sub> [30,31], were not detected in both (CNT,B)/Al composite and (Al<sub>3</sub>BC,CNT)/Al composite. However, a few sluggish humps appeared in the composites indicates there may still exist slight interface reaction. It seems that thanks to the flaky-shaped Al building blocks and providing much more available effective surface, the deeper the CNTs are embedded into the Al particles, the smaller the growth value of I<sub>D</sub>/I<sub>G</sub> ratio, indication that the better the protection of the CNTs in both (CNT,B)/Al composite and (Al<sub>3</sub>BC,CNT)/Al composite [8,32].

The images of SEM given in Fig. 3 a, b present the distribution of reinforcing phases in the matrix, in which the small-sized white

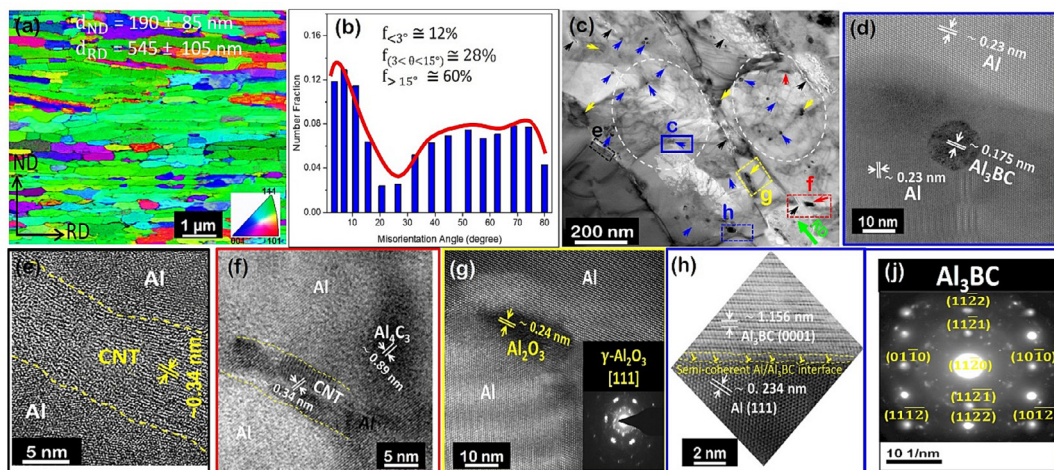
phases distributing uniformly in the Al matrix are detected to be Al<sub>3</sub>BC particles with the reference of the XRD and EDS results. High magnification image in Fig. 3c (brightfield STEM image) reveal that Al<sub>3</sub>BC particles with almost spherical morphology are estimated their size are ranging from 20 to 30 nm.

Fig. 4a demonstrates an obvious laminated structure with the measured grain sizes are 190 and 545 nm. Such an observation is more likely to associate with the reduced grain boundary mobility and the subsequent restriction of grain growth rendered by the CNTs at the GBs. Furthermore, a more of the elongated grains possess a strong <111> texture with a few grains towards the <001> direction, indicating a strong restriction of slip both in and GBs of Al grains. The presence of a laminated microstructure with 40 % of low-angle GBs (LAGBs) which in turn composed of 12 % and 28 % with  $\theta < 3^\circ$  and  $3^\circ < \theta < 15^\circ$ , are strongly effective in manifesting a strong contribution of dislocations and LAGBs strengthening respectively (Fig. 4b). Furthermore, the presence of 60 % of HAGBs mostly decorated by CNTs and some  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanoparticles are more effective in blocking slipping dislocations, thereby forcing the dislocations to tangle and accumulate grain interior and near the boundaries with a very high density about  $1.5 \times 10^{16} \text{ m}^{-2}$  (dashed ovals in Fig. 4 c).

A close look up the Fig. 4c, one can be found there are numerous spherical gray particles in size range of 6–25 nm, which are identified to be Al<sub>3</sub>BC by STEM image given in Fig. 3d. thermodynamically, having a negative formation enthalpy  $-56.34 \text{ kJ/mol}$  [33] for Al<sub>3</sub>BC compared to Al<sub>3</sub>C<sub>4</sub> ( $-36 \text{ kJ/mol}$  [33]), availability of boron atoms with carbon atoms with uncompensated high energy electron bonds at damaged CNTs tips, and amorphous carbon cover on CNTs, along with appropriate annealing heat treatment at 800°C for 3 h in flowing argon is ideal to in-situ synthesized Al<sub>3</sub>BC nanoparticles. It is expected that the formation of the Al<sub>3</sub>BC is



**Fig. 3.** The distribution of Al<sub>3</sub>BC in composite: (a) SEM image, (b) the corresponding binary image, and (c) EDS mapping incorporated into the brightfield image STEM.



**Fig. 4.** (a) EBSD image of (Al<sub>3</sub>BC,CNT)/Al laminated composite, (b) the distribution of the grain boundary misorientation angle ( $\theta$ ), (c) TEM image showing the elongated Al grains containing different reinforcing elements, (d) STEM image showing a nanoscale Al<sub>3</sub>BC in Al matrix, (e-h) HRTEM images of (e) CNT-Al interface, (f) a typical structure of CNT with small interfacial Al<sub>3</sub>C<sub>4</sub>, (g) structure of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (h) Al<sub>3</sub>BC-Al interface formed in the grain interior of Al, (i) Relative Fast Fourier transforms of Al<sub>3</sub>BC. The dashed ovals showing dislocation entanglements. The red, black, blue and yellow arrows showing Al<sub>3</sub>C<sub>4</sub>, CNTs, Al<sub>3</sub>BC and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

mainly controlled by the diffusion rate of C and B in Al matrix, which should be increased with the T in solid states, so this is more likely, no Al<sub>3</sub>BC could form during hot extrusion. As soon as boron atoms run out, a few numbers of nanorod Al<sub>3</sub>C<sub>4</sub> is formed due to exposure at high T. In other word, the Al<sub>3</sub>C<sub>4</sub> content in this study not only depends on T as previously reported by [27], but also strongly depends availability of free boron and carbon atoms. The lattice fringes of an individual Al<sub>3</sub>BC, CNT, Al<sub>3</sub>C<sub>4</sub>, and Al<sub>2</sub>O<sub>3</sub> in the composites had a spacing of  $\sim 0.175$ ,  $0.34$  nm,  $0.89$  and  $0.24$  which approximately equals to that of the (110) plane of Al<sub>3</sub>BC, (1120) plane of graphite, (003) plane of Al<sub>3</sub>C<sub>4</sub>, and (311) plane of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, respectively (Fig. 4 d-g). Thus, it can be concluded that nanoscale Al<sub>3</sub>BC with sizes of 6–25 nm respectively has been successfully synthesized in the composites. The relatively same size of Al<sub>3</sub>BC nanoparticles previously in-situ synthesized by liquid–solid reaction [29], or by self-propagating high-T synthesis [34]. Contrary to complexity and expensive the other routes proposed, the synthesized route proposed in this paper is feasible and simple in which nanoscale Al<sub>3</sub>BC is directly formed by the reaction between dissolved B and C atoms and Al matrix through ball

milling and subsequent rolling and annealing. Due to the essence of having a strong interfacial bonding, good dispersion in the Al grain interior and complete single-crystal structure of in-situ Al<sub>3</sub>C<sub>4</sub> nanorods. Furthermore, the in-situ-Al<sub>3</sub>BC/Al interface which has a semi-coherent bonding structure with orientation relationship (0111) Al<sub>3</sub>BC // (111)Al, is contained with minimum number of mismatch dislocations at the interface (Fig. 3h) in line of the results in [35,36]. Such strong bonding strength accompanied with preferred orientation of both the elongated Al grains significantly guarantee the intragranular strengthening effects of Al<sub>3</sub>BC on the elongated Al matrix. The CNTs are mostly embedded in Al matrix and aligned in the RD, signifying the existence of a strong and firm bonding between CNTs and Al matrix. The presence of a clean interface between CNT-Al with any void and interfacial product (Fig. 4 e) indicates not only a well-remaining of CNT structure with a strong bonding between Al and CNTs, but also strongly contributes in load transferring strengthening. However, small amount of nanoscale rod-like Al<sub>3</sub>C<sub>4</sub> is in-situ formed by the reaction of partially damaged CNTs with Al matrix (red arrows in Fig. 4 f). Owing to interfacial Al<sub>3</sub>C<sub>4</sub> preferentially nucleated at the open edges, so

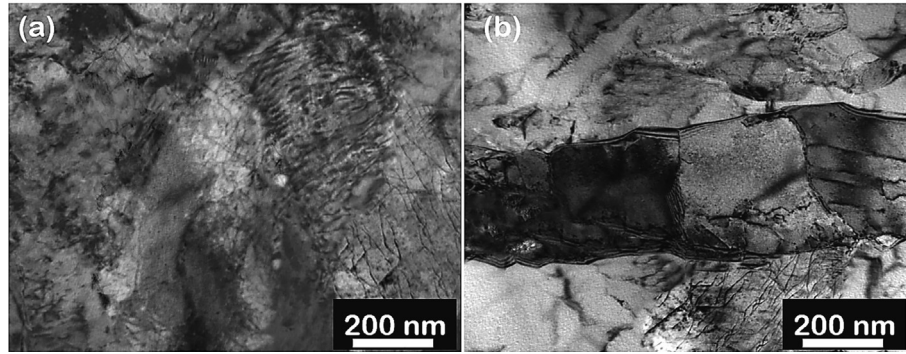


Fig. 5. TEM images of (a) Al<sub>3</sub>BC/CNT/Al and CNT/Al laminated composites, (b) CNT/Al composite; showing high density of dislocations.

Al<sub>3</sub>C<sub>4</sub> found at the open edges of CNTs which are more reactive than the CNT's parts in line of the results reported in [37,38]. It seems that the formation of Al<sub>3</sub>C<sub>4</sub> could be related to shortening and breaking of CNTs, which in turn leading to an increasing number of carbon atoms available to react with Al and B in order to produce in-situ Al<sub>3</sub>BC nanoparticles. Furthermore, some relatively spherical nanoparticles of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Fig. 4 g) both in the Al grain interior and the GBs are existed (yellow arrows in Fig. 3c) as consequence of the transformation of native amorphous(am)-Al<sub>2</sub>O<sub>3</sub> skin broken during processing at T > 450 °C [39]. Hence the oxygen introduced by the fabrication process almost effectively exists as oxides, e.g.,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Consider the native Al<sub>2</sub>O<sub>3</sub> skin on the surface of nanoflake is 4 nm

thick, the volume of Al<sub>2</sub>O<sub>3</sub> is about 2.6 vol% ( $8/300 \times 100\% = 2.6\text{ vol}\%$ ) of the total volume of 300 nm nanoflake Al powder in agreement with the value of Al<sub>2</sub>O<sub>3</sub> reported in [39]. By assuming all oxygen present is in am-Al<sub>2</sub>O<sub>3</sub> completely transformed to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> after annealing at 800°C, and also the oxygen content remains virtually unchanged after annealing. The nano-Al<sub>3</sub>BC and Al<sub>3</sub>C<sub>4</sub> play an important role for generating high effective stress via forest dislocation cutting and the Orowan strengthening, while the CNTs and nano-Al<sub>2</sub>O<sub>3</sub> effectively provide a high back stress via accumulation and hindering of dislocation annihilation at the interfaces, and GBs. Precisely, a high dislocation density ( $8.13 \times 10^{15}\text{ m}^{-2}$ ) mostly caused by inhomogeneous deformation between matrix

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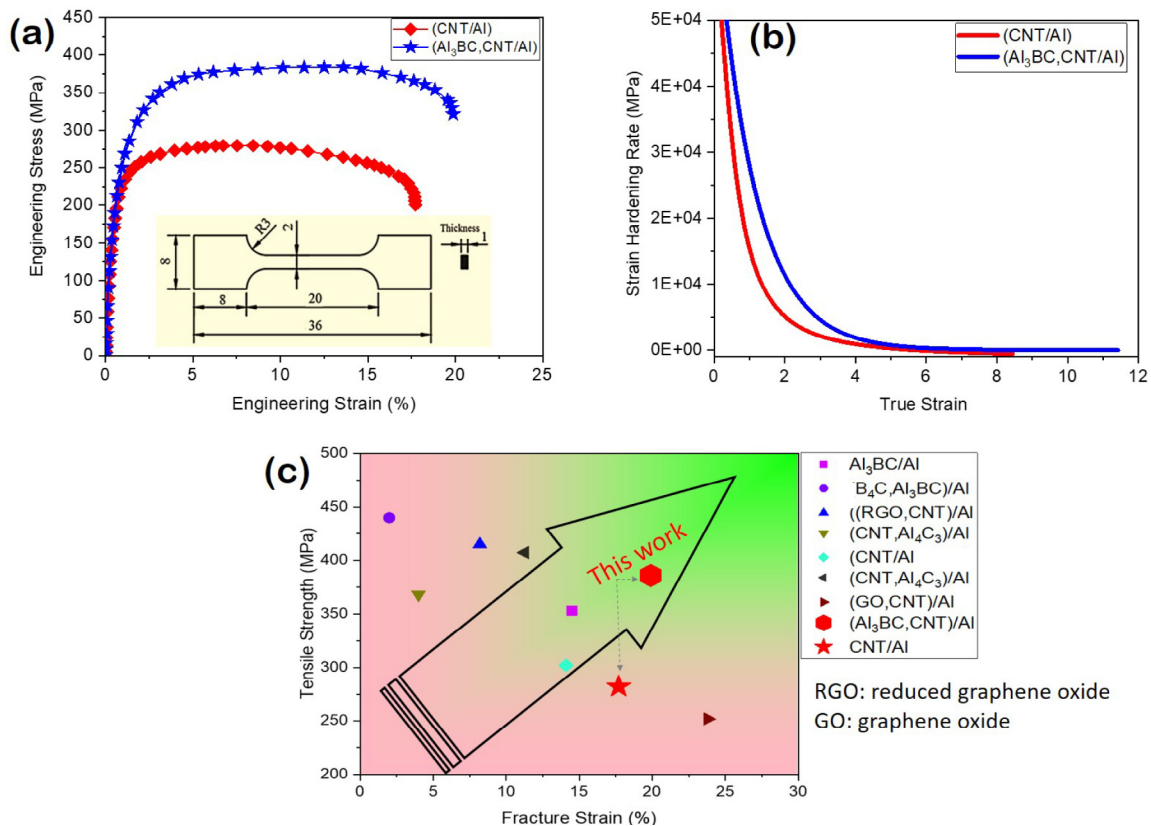


Fig. 6. (a) Engineering tensile stress–strain curves, (b) Strain hardening rate curves of Al<sub>3</sub>BC/CNT/Al and CNT/Al composites. (c) Tensile properties of aluminum composites fabricated by various solid state-based approaches [5,33,35,43–45]. The arrow showing the direction of development the stronger and tougher composites.

and reinforcements, significantly both produce the non-directional short-range local stress for a dislocation to move and dramatically provide long-range interactions with mobile dislocations, exerting a directional long-range back stress opposed to the applied stress in the case of forward loading (Fig. 5).

Shown in Fig. 6a are the tensile stress–strain curves of (Al<sub>3</sub>BC, CNT)/Al laminated and CNT/Al composites. Clearly, the (Al<sub>3</sub>BC, CNT)/Al laminated composites possess much higher strength than the CNT/Al composites due to vital intragranular and intergranular effects of reinforcements as well as laminated structure. Furthermore, Fig. 6b shows the variation of the strain hardening rate as a function of the true strain, indicating superior maintaining of a high strain-hardening rate for (Al<sub>3</sub>BC,CNT)/Al laminated composite. It is attributed to the improved dislocation storage capability of UFG Al because of both having a laminated structure and the in-situ formation of the intragranular Al<sub>3</sub>BC nanoparticles. Specifically, the (Al<sub>3</sub>BC,CNT)/Al shows a strength of 394 MPa, a uniform elongation of 13.2 % and a total elongation of 19.7 %, about 29 % of the CNT/Al in strength with an increase in total elongation from 17.7 % to 19.5 %, respectively. On the other hand, the uniform elongation of (Al<sub>3</sub>BC,CNT)/Al laminated composite is 13.2 %, while that of PM 16 vol% B4C/UFG Al with average grain size of 500 nm is only 3.5 % [40], for PM (0.5wt.%CNT, 2 vol%  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) /UFG Al with a unique intragranular dispersion of ultra-short CNTs is about 5.9 % [41]. In consideration of the similarity of the in-situ reinforcements in (Al<sub>3</sub>BC,CNT)/UFG Al and 15 vol.%Al<sub>3</sub>BC/UFG Al [35], the superior strength and ductility of (Al<sub>3</sub>BC,CNT)/UFG Al could only be attributed to the synergetic contribution of intragranular (e.g. caused by in-situ formed Al<sub>3</sub>BC, partially formed Al<sub>3</sub>C<sub>4</sub>) and intergranular strengthening (e.g. arising from CNT,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>), estimated to be 1 wt% by the spherical nanoparticles of Al<sub>3</sub>BC (Fig. 6c). A synergetic of intragranular and intergranular reinforcements in the elongated Al grains are rendered by the presence of in-situ formed nanodispersoids, which suggest the promising strengthening effects of Al<sub>3</sub>BC benefitting from the strong semi-coherent interface on the matrix. The GBs decorated by CNT and some  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is effectively lost their efficiency in dislocation annihilation by dislocation nucleation in the neighboring matrix grain near the GB, which in turn reduces the magnitude of stress concentration [42], and an increase in critical resolved shear stress as a consequence of harder dislocation motion. It supports the notion that dislocation multiplication and accumulation rather than its annihilation due to recovery was the governing mechanism.

The GBs decorated by CNT and some  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is effectively lost their efficiency in dislocation annihilation, contributing in producing of back stress hardening. While, the reinforcement settled in the Al grains interior increase dislocation blocking, and forest hardening. It is work, namely achieving ultra-high strengthening and toughening efficiency via intragranular/intergranular dispersion engineering, is one step forward from the Jiang et al. [10] work, so that the presence of the array of in-situ formed hybrid nanoparticle-rich zones surrounded by CNT-decorated GBs led to a concurrently enhancement in strength and ductility.

#### 4. Conclusions

Summarily, it is demonstrated that the unique composite, namely the (Al<sub>3</sub>BC,CNT)/UFG Al laminated composite exhibits an excellent combined strengthening-ductility effect (strength 394 MPa, elongation 19.7 %), due to the synergetic intragranular/intergranular dispersion, which stand out from most available AMCs. The interface coherency and interfacial bonding between in-situ nano-Al<sub>3</sub>BC in the interior of elongated ultrafine Al grains as well as the Al<sub>4</sub>C<sub>3</sub> formed partially at the GBs tips could provide a superior strengthening contribution compared with traditional

CNT/UFG Al composites. Through a careful combination of in situ and ex situ strengthening techniques, we provided a distribution of support, resulting in the development of dislocation blocks, stress recovery, and forest hardening. This process leads to an increase in the strength and ductility of the composite. The success of our combination and the surprising properties of this unique combination opened new opportunities for research and development of advanced materials with improved equipment and general applications.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apt.2023.104263>.

#### References

- [1] B. Sadeghi, P. Cavaliere, C.I. Pruncu, M. Balog, M. Marques de Castro, R. Chahal, Architectural design of advanced aluminum matrix composites: a review of recent developments, *Crit. Rev. Solid State Mater. Sci.* (2022) 1–71.
- [2] H. Sun, F. Saba, G. Fan, Z. Tan, Z. Li, Micro/nano-reinforcements in bimodal-grained matrix: A heterostructure strategy for toughening particulate reinforced metal matrix composites, *Scr. Mater.* 217 (2022) 114774.
- [3] F. Luo, X. Jiang, H. Sun, D. Mo, Y. Zhang, R. Shu, L. Xue, Microstructures, mechanical and thermal properties of diamonds and graphene hybrid reinforced laminated Cu matrix composites by vacuum hot pressing, *Vacuum* 207 (2023) 111610.
- [4] Z.Y. Xu, C.J. Li, Z. Wang, D. Fang, P. Gao, J.M. Tao, J.H. Yi, J. Eckert, Balancing the strength and ductility of graphene oxide-carbon nanotube hybrid reinforced aluminum matrix composites with bimodal grain distribution, *Mater. Sci. Eng. A* 796 (2020) 140067.
- [5] Z. Li, G. Fan, Q. Guo, Z. Li, Y. Su, D. Zhang, Synergistic strengthening effect of graphene-carbon nanotube hybrid structure in aluminum matrix composites, *Carbon* 95 (2015) 419–427.
- [6] L.-Y. Chen, J.-Q. Xu, H. Choi, M. Pozuelo, X. Ma, S. Bhowmick, J.-M. Yang, S. Mathaudhu, X.-C. Li, Processing and properties of magnesium containing a dense uniform dispersion of nanoparticles, *Nature* 528 (7583) (2015) 539–543.
- [7] G. Fan, Q. Liu, A. Kondo, M. Naito, K. Kushimoto, J. Kano, Z. Tan, Z. Li, Self-assembly of nanoparticles and flake powders by flake design strategy via dry particle coating, *Powder Technol.* 418 (2023) 118294.
- [8] B. Sadeghi, G. Fan, Z. Tan, Z. Li, A. Kondo, M. Naito, Smart Mechanical Powder Processing for Producing Carbon Nanotube Reinforced Aluminum Matrix Composites, *Kona Powder Part. J.* (2022) 2022004.
- [9] L. Ma, X. Zhang, B. Pu, D. Zhao, C. He, N. Zhao, Achieving the strength-ductility balance of boron nitride nanosheets/Al composite by designing the synergistic transition interface and intragranular reinforcement distribution, *Compos. B Eng.* 246 (2022) 110243.
- [10] L. Jiang, H. Yang, J.K. Yee, X. Mo, T. Topping, E.J. Lavernia, J.M. Schoenung, Toughening of aluminum matrix nanocomposites via spatial arrays of boron carbide spherical nanoparticles, *Acta Mater.* 103 (2016) 128–140.
- [11] J. Wan, J. Yang, X. Zhou, B. Chen, J. Shen, K. Kondoh, J. Li, Superior tensile properties of graphene/Al composites assisted by in-situ alumina nanoparticles, *Carbon* 204 (2023) 447–455.
- [12] Y. Zhang, X. Li, Bioinspired, graphene/Al<sub>2</sub>O<sub>3</sub> doubly reinforced aluminum composites with high strength and toughness, *Nano Lett.* 17 (11) (2017) 6907–6915.
- [13] B. Sadeghi, P.D. Cavaliere, Reviewing the integrated design approach for augmenting strength and toughness at macro- and micro-scale in high-performance advanced composites, *Materials* 16 (17) (2023) 5745.
- [14] B. Sadeghi, P. Cavaliere, Progress of Flake Powder Metallurgy Research, *Metals* 11 (6) (2021) 931.
- [15] G.L. Fan, R. Xu, Z.Q. Tan, D. Zhang, Z.Q. Li, Development of flake powder metallurgy in fabricating metal matrix composites: A Review, *Acta Metallurgica Sinica-English Letters* 27 (5) (2014) 806–815.
- [16] L. Jiang, Z.Q. Li, G.L. Fan, D. Zhang, A flake powder metallurgy approach to Al<sub>2</sub>O<sub>3</sub>/Al biomimetic nanolaminated composites with enhanced ductility, *Scr. Mater.* 65 (5) (2011) 412–415.
- [17] B. Sadeghi, P. Cavaliere, M. Balog, C.I. Pruncu, A. Shabani, Microstructure dependent dislocation density evolution in micro-macro rolled Al<sub>2</sub>O<sub>3</sub>/Al laminated composite, *Mater. Sci. Eng. A* 830 (2022) 142317.
- [18] B. Sadeghi, P. Cavaliere, C.I. Pruncu, Architecture dependent strengthening mechanisms in graphene/Al heterogeneous lamellar composites, *Mater Charact* 111913 (2022).

- [19] C. He, N. Zhao, C. Shi, S. Song, Mechanical properties and microstructures of carbon nanotube-reinforced Al matrix composite fabricated by in situ chemical vapor deposition, *J. Alloy. Compd.* 487 (1–2) (2009) 258–262.
- [20] L.P. Yan, Z.Q. Tan, G. Ji, Z.Q. Li, G.L. Fan, D. Schryvers, A.D. Shan, D. Zhang, A quantitative method to characterize the Al<sub>4</sub>C<sub>3</sub>-formed interfacial reaction: The case study of MWCNT/Al composites, *Mater. Charact.* 112 (2016) 213–218.
- [21] G. Williamson, R. Smallman III, Dislocation densities in some annealed and cold-worked metals from measurements on the X-ray debye-scherrer spectrum, *Phil. Mag.* 1 (1) (1956) 34–46.
- [22] D. Lahiri, S.R. Bakshi, A.K. Keshri, Y. Liu, A. Agarwal, Dual strengthening mechanisms induced by carbon nanotubes in roll bonded aluminum composites, *Mater. Sci. Eng. A* 523 (1–2) (2009) 263–270.
- [23] Y. Lin, B. Yao, Z. Zhang, Y. Li, Y. Sohn, J.M. Schoenung, E.J. Lavernia, Strain Energy During Mechanical Milling: Part I, Mathematical Modeling, Metallurgical and Materials Transactions A 43 (11) (2012) 4247–4257.
- [24] P.P. Chattopadhyay, I. Manna, S. Talapatra, S.K. Pabi, A mathematical analysis of milling mechanics in a planetary ball mill, *Mater. Chem. Phys.* 68 (1) (2001) 85–94.
- [25] S. Kleiner, F. Bertocco, F. Khalid, O. Beffort, Decomposition of process control agent during mechanical milling and its influence on displacement reactions in the Al–TiO<sub>2</sub> system, *Mater. Chem. Phys.* 89 (2–3) (2005) 362–366.
- [26] R. Dabouz, M. Bendoumia, L. Belaid, M. Azzaz, Dissolution of Al 6wt % mixture using mechanical alloying, *Defect and Diffusion Forum* 391 (2019) 82–87.
- [27] M. Kubota, P. Cizek, Synthesis of Al<sub>3</sub>BC from mechanically milled and spark plasma sintered Al–MgB<sub>2</sub> composite materials, *J. Alloy. Compd.* 457 (1) (2008) 209–215.
- [28] Y. Zhao, X. Ma, X. Zhao, H. Chen, X. Liu, Enhanced aging kinetic of Al<sub>3</sub>BC/6061 Al composites and its micro-mechanism, *J. Alloy. Compd.* 726 (2017) 1053–1061.
- [29] Y. Zhao, Z. Qian, X. Liu, Identification of novel dual-scale Al<sub>3</sub>BC particles in Al based composites, *Mater. Des.* 93 (2016) 283–290.
- [30] Y. Jiang, Z. Tan, G. Fan, Z. Zhang, D.-B. Xiong, Q. Guo, Z. Li, D. Zhang, Nucleation and growth mechanisms of interfacial carbide in graphene nanosheet/Al composites, *Carbon* 161 (2020) 17–24.
- [31] B. Sadeghi, P. Cavaliere, CNTs reinforced Al-based composites produced via modified flake powder metallurgy, *J. Mater. Sci.* 57 (4) (2022) 2550–2566.
- [32] H. Wei, Z.Q. Li, D.B. Xiong, Z.Q. Tan, G.L. Fan, Z. Qin, D. Zhang, Towards strong and stiff carbon nanotube-reinforced high-strength aluminum alloy composites through a microlaminated architecture design, *Scr. Mater.* 75 (2014) 30–33.
- [33] Q. Hu, W. Guo, P. Xiao, J. Yao, First-principles investigation of mechanical, electronic, dynamical, and thermodynamic properties of Al<sub>3</sub>BC, *Phys. B Condens. Matter* 616 (2021) 413127.
- [34] T. Tsuchida, T. Kan, Synthesis of Al<sub>3</sub>BC in air from mechanically activated Al/B/C powder mixtures, *J. Eur. Ceram. Soc.* 19 (9) (1999) 1795–1799.
- [35] Y. Zhao, Z. Qian, X. Ma, H. Chen, T. Gao, Y. Wu, X. Liu, Unveiling the Semicohherent Interface with Definite Orientation Relationships between Reinforcements and Matrix in Novel Al<sub>3</sub>BC/Al Composites, *ACS Appl. Mater. Interfaces* 8 (41) (2016) 28194–28201.
- [36] Y. Zhao, X. Ma, H. Chen, X. Zhao, X. Liu, Preferred orientation and interfacial structure in extruded nano-Al<sub>3</sub>BC/6061 Al, *Mater. Des.* 131 (2017) 23–31.
- [37] B. Chen, L. Jia, S. Li, H. Imai, M. Takahashi, K. Kondoh, In Situ Synthesized Al<sub>4</sub>C<sub>3</sub>Nanorods with Excellent Strengthening Effect in Aluminum Matrix Composites, *Adv. Eng. Mater.* 16 (8) (2014) 972–975.
- [38] W. Zhou, T. Yamaguchi, K. Kikuchi, N. Nomura, A. Kawasaki, Effectively enhanced load transfer by interfacial reactions in multi-walled carbon nanotube reinforced Al matrix composites, *Acta Mater.* 125 (2017) 369–376.
- [39] M. Balog, P. Krizik, M. Nosko, Z. Hajovska, M. Victoria Castro Riglos, W. Rajner, D.-S. Liu, F. Simancik, Forged HITEMAL: Al-based MMCs strengthened with nanometric thick Al<sub>2</sub>O<sub>3</sub> skeleton, *Mater. Sci. Eng. A* 613 (2014) 82–90.
- [40] X. Kai, Z. Li, G. Fan, Q. Guo, Z. Tan, W. Zhang, Y. Su, W. Lu, W.-J. Moon, D. Zhang, Strong and ductile particulate reinforced ultrafine-grained metallic composites fabricated by flake powder metallurgy, *Scr. Mater.* 68 (8) (2013) 555–558.
- [41] Q. Liu, G. Fan, Z. Tan, Q. Guo, D. Xiong, Y. Su, Z. Li, D. Zhang, Reinforcement with intragranular dispersion of carbon nanotubes in aluminum matrix composites, *Compos. B Eng.* 217 (2021) 108915.
- [42] Z. Li, L. Zhao, Q. Guo, Z. Li, G. Fan, C. Guo, D. Zhang, Enhanced dislocation obstruction in nanolaminated graphene/Cu composite as revealed by stress relaxation experiments, *Scr. Mater.* 131 (2017) 67–71.
- [43] L. Jiang, Z.Q. Li, G.L. Fan, L.L. Cao, D. Zhang, Strong and ductile carbon nanotube/aluminum bulk nanolaminated composites with two-dimensional alignment of carbon nanotubes, *Scr. Mater.* 66 (6) (2012) 331–334.
- [44] B. Sadeghi, J. Qi, X. Min, P. Cavaliere, Modelling of strain rate dependent dislocation behavior of CNT/Al composites based on grain interior/grain boundary affected zone (GI/GBAZ), *Mater. Sci. Eng. A* 820 (2021) 141547.
- [45] Z. Zhang, G. Fan, Z. Tan, H. Zhao, Y. Xu, D. Xiong, Z. Li, Bioinspired multiscale Al<sub>2</sub>O<sub>3</sub>-rGO/Al laminated composites with superior mechanical properties, *Compos. B Eng.* 217 (2021) 108916.