Original Article

Al-MWCNT nanocomposite synthesized via spark plasma sintering: effect of powder milling and reinforcement addition on sintering kinetics and mechanical properties

Lavish K. Singh, Alok Bhaduria, Tapas Laha*
Metallurgical and Materials Engineering, Indian Institute of Technology Kharagpur, Kharagpur, India

A R T I C L E   I N F O
Article history:
Received 23 November 2017
Accepted 13 March 2018
Available online 19 June 2018

Keywords:
Al nanocomposite
Multiwalled carbon nanotube
Mechanical milling
Spark plasma sintering
Sintering behaviour
Compression test

A B S T R A C T
In this work, the effect of mechanical milling of aluminium (Al) powder and subsequent addition of multiwalled carbon nanotubes (MWCNTs) as reinforcement followed by powder mixture consolidation via spark plasma sintering has been investigated. Grain growth during sintering, densification behaviour and mechanical properties (microhardness and compressive properties) were analyzed to complement the study of sintering kinetics. The results showed that for milled Al powder compact, densification started at a lower temperature as compared to the as-received powder compact. This is attributed to large specific surface area of milled Al powders and high amount of diffusivity path created during the milling. The addition of MWCNTs, reinforcement of high hardness and compressive strength, constricted Al particle deformation, sliding and rearrangement during compaction, thereby hindering densification. This behaviour was confirmed by observed increase in $T_{\text{stat}}$ and $T_{\text{end}}$, the temperature at which densification started and ended, respectively, for nanocomposites containing MWCNTs. Mechanical properties were significantly improved as a result of milling. Microhardness and compressive strength of the milled powder compact increased by 97% and 53%, respectively. MWCNTs pinned grain boundaries and caused dislocation generation and accumulation, which led to further improvement in mechanical properties. However, Al-1.0 wt% CNT showed reduction in microhardness due to inefficient dispersion of MWCNTs leading to large amounts of porosity.

© 2018 Published by Elsevier Editora Ltda. on behalf of Brazilian Metallurgical, Materials and Mining Association. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

Aluminium (Al) alloys are ideal candidates for developing light-weight high-strength metal matrix nanocomposites because of their excellent properties, such as light weight, low melting temperature, high corrosion resistance and great formability [1]. These traits are the reason for these alloys' wide application in diversified industries such as aerospace, turbines, aircraft, building materials, desalination machined components and automobiles [2]. Mechanical properties of bulk Al prepared by powder metallurgy route, can be extensively enhanced (i) by employing high energy ball milling to Al

* Corresponding author.
E-mail: laha@metal.iitkgp.ernet.in (T. Laha).

https://doi.org/10.1016/j.jmrt.2018.03.005
2238-7854/© 2018 Published by Elsevier Editora Ltda. on behalf of Brazilian Metallurgical, Materials and Mining Association. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
powder towards lowering the grain size prior to consolidation and (ii) introducing high strength nano-reinforcements such as carbon nanotubes (CNTs), which possess excellent mechanical properties, including extremely high hardness, strength, modulus of elasticity and wear resistance, combined with low density (1.8 g/cm³) [3,4].

Powder metallurgy is a widely practiced process for developing ultrafine grained and nanostructured alloys. Among different powder metallurgy consolidation techniques, spark plasma sintering (SPS) has proven to be one of the most promising techniques. SPS is a powder consolidation process based on the simultaneous application of low-voltage, high-energy pulse current and uniaxial pressure [5,6], which allows the production of high density components at lower temperature and in a shorter time than the conventional sintering processes. This sintering process also assures uniform and homogeneous microstructure in the whole volume of sintered materials [7]. These benefits render SPS suitable for development of various novel materials, such as high density ceramics [8,9], bulk nanocrystalline materials [10], functionally graded materials [11], nanocomposites [12] and bulk metallic glasses [13,14], which are difficult to be produced by traditional sintering methods.

There are different factors which extensively influence the sintering behaviour of metallic powders when they are consolidated via different sintering techniques. Ball milling of powders, usually performed to enhance the mechanical properties, is one of the most important factors that affects the sintering kinetics. For ball milled powders, specific surface area increases and the thermodynamic driving force for sintering is proportional to the specific surface area of the powder [15]. Milling of powders also influences the number and area of the contact points and, in turn, the local pressure and the current density, which are of great importance in heat generation during SPS [15,16]. Libardi et al., while performing SPS of FeMo powders, observed that the temperature at which densification started reduced from 510 to 420 °C upon milling for 20 h [10]. Study on the sintering behaviour of Y2O3 stabilized ZrO2 nanoparticles has shown that the sintering initiated at a temperature, which is 200 °C lower than that for micron sized ZrO2 particles [17–19]. Similar observation was also reported by Guyon et al. and Fasebani et al. while studying the sintering kinetics of Ti-43.7Al-1.9Cr-2.0Nb and Fe-14Cr-1Ti-0.3Mo-0.5La2O3, respectively [20,21]. However, no significant study has been conducted to analyze the effect of milling of Al powders on sintering kinetics. There has been extensive study on CNT reinforced Al based nanocomposites in terms of microstructure and mechanical properties but there has been no detailed study on the effect CNT addition in Al powders in terms of sintering kinetics [3,22]. Libardi et al. reinforced 1.5 wt% SiO2 in ball milled FeMo powders and observed an increase in the temperature from 420 to 560 °C at which the densification started [10].

In the present work, the effect of milling and reinforcement, multiwalled carbon nanotubes (MWCNTs), on the sintering behaviour of Al powder has been studied. Al powder was milled via high energy ball milling and in order to study the effect of reinforcement on sintering kinetics, milled Al powder was reinforced with varying content (0.5 and 1.0 wt%) of MWCNTs and the resultant powder mixture was spark plasma sintered. Crystallite size variation during sintering, densification behaviour and mechanical properties (microhardness and compressive properties) were analyzed in the present work to study the effect of sintering kinetics.

2. Experimental procedure

2.1. Materials processing

Commercial gas atomized Al powder of purity 99.5%, procured from Alfa Aesar, USA, was used as the matrix material for synthesizing the compacts and MWCNTs of purity >95%, 40–70 nm in diameter and 0.2–0.5 μm in length were used as reinforcement. High energy ball milling was employed in order to transform initial microcrystalline Al powders to nanocrystalline Al powders. The powders were ball milled in a planetary ball mill (PM 200, Retsch GmbH, Germany) in hardened steel vials (125 ml capacity) using 10 mm diameter hardened steel balls for 10 h at 180 rpm with ball to powder ratio (BPR) of 20:1. Automatically controlled rotating disc in the planetary ball mill was given 15 min break after every 30 min of alternate clockwise and ant clockwise rotations to avoid excessive heating of powders during milling. Toluene was used as the process control agent (PCA) to restrict powder agglomeration and avoid air contamination. Powder handling was carried out in a glove box (Labstar, M-Braun Inertgas-Systeme GmbH, Germany) to avoid air contamination. The as-received MWCNTs were highly entangled and agglomerated due to high aspect ratio and strong van der Waals force of attraction among CNTs [3,23]. One of the most widely used methods to disperse CNTs is functionalization. Functionalization of CNTs consists of attachment of organic or inorganic moieties to their tubular structure, which modulates their physicochemical properties, increasing their ease of dispersion, manipulation, and processability, among others. In the present work, MWCNTs were physio-chemically functionalized via nitric acid (HNO3) and sodium dodecyl sulfate (SDS) prior to mixing with Al powders. Introduction of oxygen containing functional groups on MWCNTs via HNO3 is recognized as an efficient method for CNT purification, promoting dispersion and surface activation at the same time [24]. Surfactants such as SDS produce an efficient coating and induce electrostatic and/ or steric repulsions that counter balances van der Waals attractions between CNTs, which is one of the main reasons for entanglement of CNTs [25]. MWCNTs were initially ultrasonicated for 4 h in 68% concentrated HNO3, and the suspension was filtered and neutralized with NaOH pellets (0.15–0.2 g, each) in the ratio of 1 pellet to 100 ml of distilled water. The CNTs were then subjected to repeated rinsing with distilled water until a pH value of 7 was attained. The suspension was then filtered and dried at 110 °C for 2 h to remove the moisture. HNO3-treated (chemically functionalized) CNTs were mixed with SDS in 2:3 weight ratio followed by ultrasonication for 4 h. The obtained suspension was again filtered and dried at 110 °C for 2 h. Fig. 1 shows the morphology and dispersion of MWCNTs in ethanol before and after functionalization. It can be clearly seen that the functionalized CNTs are homogeneously dispersed as compared to the pristine CNTs. Several other authors have used various functionalization techniques
to obtain homogeneous dispersion of CNTs [3,26,27]. Al powders (both as-received and ball milled) and mixtures of milled Al powders and physio-chemically functionalized CNTs (0.5 and 1.0 wt%) were consolidated separately by SPS (Model SPS 625, Fuji Electronic Industrial Co. Ltd., Japan) in a cylindrical graphite die/punch set of 10 mm internal diameter at 550 °C with a heating rate of 50 °C/min for 20 min holding time at 80 MPa pressure under argon atmosphere to make 10 mm diameter discs of ~5 mm thickness.

2.2. Characterization

Scanning electron microscopy (SUPRA 40, Carl ZEISS SMT, Germany) and transmission electron microscopy (JEM-2100 LaB₆, 200 kV, JEOL Inc., USA) were used to study the microstructural and morphological features of the SPS consolidated samples. Energy Dispersive Spectroscopy (EDS), coupled with SEM was used to estimate the oxygen in the powders. X-ray diffraction (PW 1710, PHILIPS, Netherlands) was carried out using Cu-Kα radiation (wavelength of 1.54 Å) at an operating voltage of 40 kV. The density of the samples was determined using a density determination kit (Satorius YDK03) based on Archimedes’ principle where deionized water was used as the liquid medium. Specific surface area of the as-received and milled Al powders was measured by a powder surface area analyzer (Nova 25 E-series, Quantachrome Instruments, USA) after degassing of the powders. Vickers microindenter (UHLMHT - 001, Walter Uhl, Germany) was operated with a load of 25 gf and a dwell time of 10 s to evaluate the microhardness of the sintered samples. Compression test was performed using a universal tensile testing machine (Instron 1344 machine) at a strain rate of 60 × 10⁻³ min⁻¹. Cylindrical samples of dimension Ø3 × 5 mm were prepared for the compression test as per ASTM E9 standards. Five samples of each composition were tested for the compression test.

3. Results and discussion

3.1. Crystallite size variation

SEM images of as-received (unmilled) and ball milled Al powder particles are shown in Fig. 2a and b, respectively. As a result of ball milling, the morphology of the Al powders changed from conically/ellipsoidally elongated and spherical particles of various sizes (7–15 μm) to flaky and irregular shaped...
powders. Upon milling, the oxygen content analyzed by EDS in the powders increased from 1.18 wt% to 3.67 wt% (Table 1). The source of oxygen contamination in the milled powder could be the milling media and milling atmosphere [28]. The XRD patterns of the as-received and ball milled Al powders, sintered Al compacts and Al-CNT nanocomposites with varying CNT content (0.5 and 1.0 wt%) are shown in Fig. 3. XRD spectra of the powders and synthesized composites show the presence of Al and did not reveal formation of any new phase such as oxide or carbides of Al. The crystallite size (d) was calculated from the XRD patterns by applying the following modified Williamson–Hall equation [29] and is reported in Table 2.

$$\rho_{\text{Al}} \cdot \cos \theta = \frac{K\lambda}{d} + 4\varepsilon \cdot \sin \theta$$  \hspace{1cm} (1)$$

where $\rho_{\text{Al}} = \sqrt{(\rho_{\text{Al}})_{\text{measured}} - (\rho_{\text{Al}})_{\text{instrumental}}}$ is the broadening after incorporation of the instrumental broadening, $(\rho_{\text{Al}})_{\text{measured}}$ and $(\rho_{\text{Al}})_{\text{instrumental}}$ are the full width half maxima (FWHM) of the maximum intensity peak (peak position $\theta$) for the experimental and standard sample (strain free annealed pure Al sample), respectively. K is a constant, $'\lambda'$ is the wavelength of the X-ray used and $'\varepsilon'$ is the induced lattice strain. The crystallite size of the Al powders reduced from 422 nm to 38 nm after the milling (Table 1). Upon sintering the as-received and milled Al powders, the crystallite size increased to 502 nm and 81 nm, respectively. The increase in crystallite size is not very significant owing to the faster sintering kinetics of SPS. The addition of CNTs into milled Al powders resulted in reduction of crystallite size as deduced from the XRD patterns of the nanocomposites. As can be seen in Table 2, the crystallite size of Al-0.5 wt% CNT is 66 nm, which is further reduced to 57 nm for Al-1.0 wt% CNT.

TEM images of Al-0.5 wt% CNT nanocomposite are shown in Fig. 4. The image in Fig. 4a clearly exhibits the presence of nanocrystalline and sub-micron size grains in the nanocomposite after consolidation. As the sintering of the Al powders proceeded, two opposite phenomena took place and the balance between these two processes determined the final grain size in the sintered compacts. On one hand during sintering, dislocation rearrangement took place which resulted in sub-grain formation. Fig. 4b shows the TEM image of sub-grains formed in Al-0.5 wt% CNT nanocomposite. These sub-grain boundaries then developed into high-angle grain boundaries, resulting in grain refinement. On the other hand, dynamic recovery and recrystallization reduced the dislocation density.

### Table 1 – Oxygen content, crystallite size, specific surface area, green density (at sintering pressure) and dislocation density of the as-received and milled Al powder particles.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Oxygen content (wt%)</th>
<th>Crystallite size (nm)</th>
<th>Specific surface area (m²/g)</th>
<th>Green density (%)</th>
<th>Dislocation density (m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received Al powder</td>
<td>1.18</td>
<td>422</td>
<td>0.226</td>
<td>91</td>
<td>3.25 × 10¹⁴</td>
</tr>
<tr>
<td>Milled Al powder</td>
<td>3.67</td>
<td>38</td>
<td>16.667</td>
<td>88</td>
<td>2.05 × 10¹⁵</td>
</tr>
</tbody>
</table>

### Table 2 – Crystallite size, relative density, densification start and finish temperatures, maximum displacement rate temperature, yield strength and compressive strength (at 20% elongation) of the Al compacts and Al-CNT nanocomposites.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Crystallite size (nm)</th>
<th>Relative density (%)</th>
<th>$T_{\text{start}}$ (°C)</th>
<th>$T_{\text{finish}}$ (°C)</th>
<th>$T_{\text{max}}$ (°C)</th>
<th>Compressive strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al_{unmilled compact}</td>
<td>502</td>
<td>99.8</td>
<td>65</td>
<td>407</td>
<td>368</td>
<td>153</td>
</tr>
<tr>
<td>Al_{milled compact}</td>
<td>81</td>
<td>98.9</td>
<td>31</td>
<td>302</td>
<td>200</td>
<td>234</td>
</tr>
<tr>
<td>Al_{milled-0.5 wt% CNT}</td>
<td>66</td>
<td>98.2</td>
<td>39</td>
<td>447</td>
<td>204</td>
<td>256</td>
</tr>
<tr>
<td>Al_{milled-1.0 wt% CNT}</td>
<td>57</td>
<td>97.1</td>
<td>62</td>
<td>499</td>
<td>211</td>
<td>–</td>
</tr>
</tbody>
</table>
and could increase the grain size. With the incorporated CNTs, the dislocation motion could be blocked at Al-CNT interfaces, which would enhance the dislocation accumulation. Consequently, addition of 0.5 wt% CNTs led to decrease in crystallite size in the sintered nanocomposite from 81 nm (in milled Al powder compact) to 66 nm. Fig. 4c shows the dislocation tangles present in Al-0.5 wt% CNT nanocomposite. Besides, the MWCNTs and its clusters exert pinning effect which further resists grain growth [24].

High energy ball milling causes a drastic increase in dislocation density resulted by severe plastic deformation in strain-hardenable materials. The dislocation density ($\rho_d$) for as-received and ball milled Al powders was estimated according to the following equation, based on the lattice strain and crystallite size values [30]:

$$\rho_d = \frac{2\sqrt{3}(\epsilon^2)^{3/2}}{b'd}$$  \hspace{1cm} (2)

where $(\epsilon^2)^{1/2}$ is average lattice strain and ‘b’ is Burgers vector = 0.286 nm [31] and ‘d’ is the crystallite size. It was calculated that, the increased amount of cold working led to increase in dislocation density from $3.25 \times 10^{14}$ m$^{-2}$ for as-received Al powders to $2.05 \times 10^{15}$ m$^{-2}$ for ball milled Al powders.

3.2. Densification of the sintered compacts

Green density of the as-received Al powder compact ($\text{Al}_{\text{unmilled}}$) and ball-milled Al powder compact ($\text{Al}_{\text{milled}}$) was estimated by applying a uniaxial pressure of 80 MPa, which was the pressure applied during SPS in the present study, for 2 min. $\text{Al}_{\text{milled}}$ compact showed lower green density (87.6%) as compared to the $\text{Al}_{\text{unmilled}}$ compact (91.1%). Powder compaction at a high pressure of 80 MPa involved a certain amount of sliding and rearrangement of individual particles, both of which became increasingly difficult for strain-hardened lower-size milled particles. Besides, the frictional force between ball milled particles became a very significant obstacle to the relative motion and rearrangement of the finer particles owing to increased surface area of the milled powders. Also, the irregular shape of milled powders further hindered the flowability of the particles. This difference in green density was translated in final density of the sintered Al compacts. The dislocations in plastically deformed crystals, both geometrically necessary and statically stored may also increase the volume of a nanocrystalline material and thus decrease its density [30]. All these factors contribute to the formation of green bodies with a lower density for ball milled powders. Table 2 presents the relative density of the sintered Al compacts and Al-CNT nanocomposites. It can be observed that

![TEM images showing (a) retention of nanocrystalline Al grains post sintering, (b) sub-grain formation, and (c) dislocation tangles present in the Al-0.5 wt% CNT nanocomposite.](image-url)
as the CNT content was increased, the relative density of the nanocomposites decreased.

Due to the large difference in hardness and compressive strength values of Al and CNTs, the later particles act as a barrier to the rearrangement, deformation and diffusion of Al particles, thereby, hindering densification. This leads to higher porosity in nanocomposites with higher CNT content, irrespective of the sintering conditions. Fig. 5a shows SEM micrograph of Al-0.5 wt% CNT nanocomposite. Owing to physio-chemical functionalization treatment of MWCNTs and low reinforcement content in the matrix, Al-0.5 wt% CNT nanocomposite exhibited efficient and homogeneous consolidation. When 1.0 wt% CNT was added to the matrix, agglomeration of CNTs took place in spite of functionalization. This resulted in segregation of CNT bundles at the interparticle boundaries which inhibited the diffusion mechanism, rendering increased porosity and decreased relative density. Fig. 5b shows the SEM image of Al-1.0 wt% CNT, where porosities can be clearly seen. Several researchers have reported similar trend of CNT aggregates inhibiting diffusion, thereby, hindering densification irrespective of the matrix or the processing technique used for consolidation [32-34]. Zheng et al. fabricated Cu-CNT coatings and observed that the porosity of ball milled copper (Cu) increased from 13.84% to 21.68% upon introduction of 5 vol% CNT [33]. In the present study, Fig. 5c shows the agglomeration of CNTs between the interparticle boundaries in Al-1.0 wt% CNT nanocomposite. CNTs being extremely strong in compression as compared to Al, when agglomerated, got entrapped in between the Al powder particles and resisted sintering to such an extent that small pits were formed (Fig. 5d). Fig. 6 shows TEM image of CNT reinforced nanocomposites. As can be seen clearly, the CNTs are well dispersed in Al-0.5 wt% CNT, whereas, it is extensively agglomerated in Al-1.0 wt% CNT.

3.3. Sintering behaviour of as-received and ball-milled Al powders

In order to study the sintering kinetics in SPS, variation in the movement of punch within the powder-filled die with respect to sintering temperature was continuously recorded. Fig. 7a depicts the variation in punch displacement with sintering temperature, whereas, Fig. 7b presents the variation in punch displacement rate with the sintering temperature. The variation in the curve can be categorized into three different stages. The first stage reflects the initial period where the rearrangement of powders took place and the densification might be due to only neck growth initiation. The intermediate stage, where the punch displacement rate increased rapidly irrespective of the state (as-received or milled) of the powders, might be due to concurrent particle consolidation and reduced number of interconnected pores. However, the punch displacement rate increased very rapidly for milled Al powders as compared to that of as-received powders. The final stage of densification showed significant drop in the rate of densification as the pores in the compact would have been nearly closed in the intermediate stage. In the final stage, for as-received Al powder compact, even if the temperature was increased further (beyond 408 °C), no more variation in punch displacement was observed, implying that no further increase in density occurred. However, in case of Al\textsubscript{milled} compact, even in the later stage the displacement kept on increasing, but the rate of increase in displacement diminished significantly. The rate of densification slowed down as relative density approached
the theoretical during the final stage of sintering. Fig. 7b confirms that the rate of punch displacement reduced drastically for Al\textsubscript{milled} compact once the plateau region was crossed. The variation in punch displacement rate with sintering temperature can be attributed to (i) the rearrangement of powders, (ii) localized deformation, (iii) core/bulk deformation and (iv) porosity annihilation [16].

From the displacement curve it is possible to determine the temperature at which densification started (T\textsubscript{start}) and ended (T\textsubscript{end}) and the displacement rate curve displays the temperature at which maximum sintering rate (T\textsubscript{max}) was achieved. The data are summarized in Table 2. For milled Al powder based nanocomposites, T\textsubscript{end} has been considered as the temperature corresponding to 1.75 mm, of punch displacement, since the saturation density was never approached when milled Al powders were sintered. For Al\textsubscript{milled} compact, the densification started at a lower temperature as compared to the Al\textsubscript{unmilled} compact, which underwent large displacement before the sintering began. Higher T\textsubscript{start} and lower total displacement values during sintering of Al\textsubscript{unmilled} compact can be attributed to the lower density of dislocations and grain boundary and other microstructural defects in unmilled powder particles as compared to those in the milled powders [10,21]. For Al\textsubscript{milled} compact, high diffusivity paths created during heavy plastic deformation enhanced sintering efficiency, which contributed to lower T\textsubscript{start} [21]. Also, a large specific surface area of Al powder particles post milling activated the surface diffusion mechanism at the initial stage of sintering, which contributed to lower T\textsubscript{start}. The specific surface area of Al powder particles, as measured by powder surface area analyzer increased from 0.226 m\textsuperscript{2}/g to 16.667 m\textsuperscript{2}/g upon milling. Also, particle surfaces are known to have a higher concentration of defects and dangling metallic bonds than the interior of the particles. As a result, the atomic mobility on the particle surface was higher. Surface of milled Al particles took up a much larger fraction of the total sintering system than as-received powders. Collectively, milled Al powder particles demonstrated a more activated sintering behaviour and therefore, exhibited a much earlier onset of sintering.

The punch exhibited intense displacement for as-received powder particles before densification-start temperature. This was due to lower hardness and less complicated geometrical shape of the unmilled powder particles, which facilitated rearrangement of the particles to a better packed powder
compact [21]. On the contrary, milled Al powders exhibited complicated geometrical shape and higher hardness [39] and therefore, the punch underwent less displacement before the densification-start temperature. Fig. 7a also reveals that although compacts containing milled Al powders never reached its saturation density, following which the density does not increase further irrespective of an increase in sintering temperature, yet major part of the achievable density was attained at a much lower temperature. The value of \( T_{\text{max}} \), as shown in Table 2, reduced significantly from 368 °C for \( \text{Al}_{\text{milled}} \) compact to 211 °C for \( \text{Al}_{\text{unmilled}} \) compact. Significantly higher value of maximum displacement rate for milled Al powders as compared to the unmilled Al powders further complemented the more activated sintering behaviour of ball milled Al powders.

3.4. Sintering behaviour in CNT added Al powders

Punch displacement versus sintering temperature and punch displacement rate versus sintering temperature curves of CNT reinforced Al nanocomposites followed the same trend as the \( \text{Al}_{\text{milled}} \) compact irrespective of the content of reinforcement. However, the punch displacement for CNT reinforced nanocomposites lagged behind the \( \text{Al}_{\text{milled}} \) composite. Moreover, as the CNT content in the compact was increased from 0.5 wt% to 1.0 wt%, the lag in the punch displacement became more apparent. From Fig. 7a it can be seen that with the addition of MWCNTs, \( T_{\text{start}} \) and \( T_{\text{end}} \) increased. With respect to \( \text{Al}_{\text{milled}} \) nanocomposite, the \( T_{\text{start}} \) is increased by 26% for Al-0.5 wt% CNT, which is further increased by 100% for Al-1.0 wt% CNT. Similarly, \( T_{\text{end}} \) is increased by 48% and 65%, respectively. This behaviour is attributed to hard and high compressive strength of CNTs, which constricted Al particle deformation, sliding and rearrangement during compaction. The harder CNT particles as compared to Al powder particles caused friction during the compaction process. Further, interparticle friction can occur between the CNTs, between the Al particles and CNT as well as between both these constituents and the die walls. Also, the CNTs and its agglomerates enveloped the Al powder particles to certain extent decreasing the contact area between Al powder particles. This hindered the neck formation by causing restriction to atomic diffusion. Moreover, the grain boundary pinning effect not only inhibits the grain growth, but also increases the activation energy for all the diffusion controlled process like sintering [10]. Overall, the presence of CNTs in Al powders seems to be hindering the sintering process between the Al particles leading to a less densified structure. Fig. 7b shows shift in \( T_{\text{max}} \) to a higher value as the CNT content increased. Also, the value of maximum displacement rate gradually reduced with increasing CNT content. These observations complement the earlier observation that addition of MWCNTs in Al powders hinders densification.

3.5. Mechanical properties

Fig. 8 displays the variations in microhardness values and uniaxial compressive stress-strain response of various SPS compacts. The compression samples were tested to a predetermined maximum strain of 20%. The compressive strength values of the samples are tabulated in Table 2. Mechanical properties of the sintered compacts are significantly affected by the density and porosities present in the sample. However, considering the \( \text{Al}_{\text{unmilled}} \) and \( \text{Al}_{\text{milled}} \) compacts, the latter showed significant improvement in the mechanical properties in spite of slightly lower densification. The microhardness increased from 36 VHN to 71 VHN. This is due to the fact that the difference in densification was not very pronounced. Addition of CNT reinforcement into the matrix further enhanced the mechanical properties. Microhardness and compressive strength increased by 17% and 10%, respectively upon addition of 0.5 wt% CNT into the milled Al matrix. The presence of CNTs in the matrix led to grain refinement in a number of ways. CNTs, apart from acting as a second phase, increased work hardening and thermal conductivity. All these variations collectively led to increased nucleation rate during recrystallization processes leading to finer grain structure, thereby, providing Hall–Petch strengthening [36].

An identical relation, which was observed in the microhardness values of the various compacts, also was observed in the compression test properties. A major factor that contributes to the enhancement of mechanical properties of the milled Al powder consolidated composites is the lattice strain present in the samples. Due to significant mismatch in the coefficient of thermal expansion of Al (23.6 K\(^{-1}\)) and MWCNT (1K\(^{-1}\)), an increase in lattice strain during sintering of powder mixture occurs, which leads to increase in dislocation density [37]. This accumulation of disloca-

![Fig. 8](image)

**Fig. 8** - (a) Microhardness and (b) uniaxial compressive stress-strain response of the various SPS compacts.
tions ultimately contributes to the overall strength of the nanocomposites. However, Al-1.0 wt% CNT nanocomposite displayed inferior microhardness (73 VHN) as compared to Al-0.5 wt% CNT nanocomposite (83 VHN). Also, the former composite fractured during the compression test even before reaching the predetermined strain of 20%, which rendered the composite of no practical importance. This was attributed to the inefficient dispersion of CNTs within the matrix and high porosity content in the composite. Fig. 9 shows SEM images of the sample surface post compression test. The surface of Al-0.5 wt% CNT showed no sign of cracks and pits, whereas, the fractured surface of Al-1.0 wt% CNT exhibited cracks propagated throughout the samples. These cracks would have initiated due to the stress concentration exerted at the porosities while performing the compression test. The inset in Fig. 9b clearly shows extensive agglomeration of CNTs within the cracks present in Al-1.0 wt% CNT. Therefore, the mechanical properties of Al\textsubscript{milled} compact was significantly enhanced by the addition of MWCNTs up to 0.5 wt%, beyond which the addition proved to be detrimental for the mechanical properties.

4. Conclusions

The conclusions that can be drawn from the results presented in this work are as follows.

- The addition of CNTs into milled Al matrix powders resulted in reduction of crystallite size. This reduction was attributed to generation and accumulation of dislocations as a result of CNT addition and the pinning effect exerted by the CNTs and their clusters. Al\textsubscript{milled} compact had a low green density (87.6%) as compared to the Al\textsubscript{unmilled} compact (91.1%). The difference in green density was also translated in the final density of the sintered specimen and the densification further reduced for CNT added nanocomposites.
- Punch displacement with respect to sintering temperature during sintering of as-received and ball milled Al powders followed the same trend, i.e., the displacement increased slowly at the beginning of the heating followed by a rapid increase in displacement until a plateau was reached. In the later stage, for Al\textsubscript{unmilled} compact the density does not increase further. However, in case of Al\textsubscript{milled} compact, even in the later stage the punch displacement kept on increasing but the rate of increase in displacement diminished significantly. Also, for Al\textsubscript{milled} compact, the densification started at a lower temperature as compared to the unmilled counterpart. With the addition of CNTs, T\textsubscript{start} and T\textsubscript{end} increased and a lag was seen in punch displacement rate vs. sintering temperature graph. This behaviour was attributed to hard and high compressive strength of CNTs which constricted Al particle deformation, sliding and rearrangement during compaction.
- Mechanical properties of the sintered specimens improved by the collective effect resulted from porosities, crystallite size and dislocation density. Al\textsubscript{milled} compact exhibited significantly improved microhardness and compressive strength as compared to the as-received powder compact. The mechanical properties were further enhanced upon CNT addition by virtue of grain boundary pinning and associated dislocation generation and accumulation. However, Al-1.0 wt% CNT showed deterioration in microhardness due to inefficient dispersion of CNTs within the matrix leading to porosity in the matrix.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgement

The authors acknowledge the “SERC Funding” from Department of Science and Technology, Government of India (SERC/ET-0388/2012) for providing the financial support.

References


