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Synthesis of WS₂/CNT hybrid nanoparticles for fabrication of hybrid aluminum matrix nanocomposite

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Abstract
In this study, a simple, safe and cost-effective method was developed for fabricating the tungsten disulfide/carbon nanotube (WS₂/CNT) hybrid nanoparticles via chemical vapor deposition (CVD) process. Hybrid nanoparticles used for reinforcing the aluminum matrix. The hybrid nanocomposites were prepared by powder metallurgy processing and consolidated by the Hot-Pressing process. The chemical composition and morphology of the WS₂/CNT hybrid particles were studied by x-ray diffraction (XRD), filed emission scanning electron microscopy (FESEM), Raman spectra, Fourier-transform infrared spectroscopy (FTIR) and thermo gravimetric analysis (TGA). The results proved that the uniform, pure and tubular WS₂/CNT hybrid nanoparticles were produced and WS₂ nanoparticles were decorated the CNT surface successfully. Optical microscopy (OM) and FESEM used for characterization of the microstructure of hybrid nanocomposite, indicate a good distribution of hybrid nanoparticles in the aluminum matrix. Maximum values of relative density, hardness and compressive strength were measured for sample with WS₂/CNT ratio of 1:1. A relative density of more than 99.5% was obtained for this sample. Hardness and compressive strength were improved by 43% and 60% compared with pure aluminum respectively.

1. Introduction

Hybrid metal matrix composites (HMMCs) are the next generation of metal matrix composites that are reinforced with two or more reinforcing phases with different type, morphology or size. The combination of different reinforcements in a hybrid composite leads to better properties than conventional composites with single reinforcement [1]. Hybrid aluminum matrix nanocomposites have been considered to increase strength and toughness simultaneously, controlling the corrosion and lowering the costs in recent years. Some of the nano and micro particles used as a reinforcing agents in aluminum matrix are (SiC, Al₂O₃, graphite, SiC), (graphite, Al₂O₃), (WS₂, SiC) and (CNT, Al₂O₃) [2–5]. Various methods have been used for fabricating the aluminum hybrid nanocomposites. One of the most common methods of preparing these nanocomposites is mechanical grinding. In this method, due to the low processing temperature, the destructive reactions in the structure are prevented and the particles exhibit a more uniform and homogeneous distribution in the structure [6]. In the last decade carbon nanotube and tungsten disulfide have been used individually as the reinforcement for aluminum matrix. Kuzumaki et al [7] have shown that tensile strength doubles with the addition 10 vol% of CNT to the aluminum matrix. Researchers have attempted to add up to 6.5 vol% of CNT into aluminum matrix by powder metallurgy. The maximum tensile strength increment of 129% has been reported to be for addition 5 vol% of CNT. At higher volumes fraction of CNT, agglomeration areas appear and these weak joint segments reduce mechanical properties. Tungsten disulfide nanoparticles have also been used in recent years to enhance the mechanical and tribological properties of metal matrices such as magnesium [8, 9], copper [10] and aluminum [11, 12]. Ranjifo et al [11] investigated the effect of adding tungsten disulfide nanoparticles to the
aluminum on tribological behavior at ambient temperature and 200 °C. The relative density of nanocomposites was reported 99% wht addition of 2 vol% of tungsten disulfide. This is due to the filling of the cavities between the aluminum particles by tungsten disulfide nanoparticle. Wear test results show a 50% reduction in friction coefficient at room temperature and 200 °C. In order to improve the wear properties of aluminum for use in automobiles, Neustadt et al.[12] have added microplates and fullerene-like tungsten disulfide to the aluminum matrix up to 20 wt%. The results show that tungsten disulfide flakes have improved the hardness and wear resistance of aluminum compared to fullerene-like particles. The reduction of the friction coefficient for the fullerene-like nanoparticles and microplates were 20% and 30%, respectively.

WS₂/CNT hybrid particles have been considered recently[13–15]. CNT is highly regarded for hybridization with other materials. The internal cavity of nanotubes is a good place to encapsulate other compounds and structures. In addition, the surface of CNT is a proper site to connect to other materials[13]. CNT, cannot be well distributed in metal matrix. The hybridization of CNT with other reinforcements such as WS₂ results in its better distribution in metal matrix[14]. Li et al.[13] used CVD process for producing hybrid particle. they dispersed CNT in a para-tungsten solution and synthesized tungsten oxide nanoparticles on CNT. The sulfurization of hybrids made in a quartz reactor using H₂S gas. Eventually WS₂/CNT hybrid synthesized successfully by this approach. CVD is a general method for the production of CNT, fullerene-like and nanotube of tungsten disulfide and WS₂/CNT hybrid nanoparticle. H₂S gas as a source of sulfur has been used in CVD process in many research[13–20]. But H₂S is very toxic and some researchers tried to remove it from the process[21–29].

The main aim of this work is to remove the H₂S from the process and to develop an easy, safe and inexpensive route for the production of WS₂/CNT hybrid nanoparticle. In this route, the toxic hydrogen sulfide gas is replaced with the sulfur powder in the sulfidation process. In this research Al/WS₂–CNT hybrid nanocomposite is produced by employing mechanical milling and hot pressing. Finally, the microstructural and mechanical properties of the hybrid nanocomposite are investigated. To the best knowledge of the authors, the addition of WS₂/CNT hybrid particles to aluminum matrix and the study of its mechanical properties have never been reported in the literature.

### 2. Materials and methods

#### 2.1. Materials

The Aluminum powder with 99% purity was purchased from Khorasan Powder Metallurgy Co.Ltd. The aluminum powder had a spherical morphology wit a particle size <20 μm. Multi-walled carbon nanotubes had an over 95% purity (outer diameter = 10–20 nm, inner diameter = 5–10 nm and length =10–30 μm) provided by Iran Research Institute of Petroleum Industry. Tungsten three oxide nanoparticles with particle size below 50 nm, Sulfur powder, Ethanol and Acetone with purity of 99% was supplied by Merck. The chemicals were used as received with no further purification.

#### 2.2. Synthesis of hybrid nanoparticle

First, the CNTs were dispersed in 200 cc of Ethanol by sonication for 30 min. Tungsten oxide nanoparticles were then added to this solution and sonicated for 4 h. Finally, the solution was stirred at 70 °C for 30 min until it became paste. The final paste was dried in a vacuum oven at 80 °C for 4 h. The carbon nanotube/tungsten three oxide hybrid powder, as well as the sulfur powder were transferred to the quartz reactor in a PA-CVD reactor with two thermal zones. Sulfur powder placed in first zone with targeted temperature of 400 °C and the carbon nanotube/tungsten three oxide hybrid powder placed in the second zone with a targeted temperature of 800 °C. A vacuum of 10⁻³ mbar was applied, and then argon and hydrogen gases were blown into the reactor, respectively. The ratio of hydrogen/argon is considered to be 1 to 3 and the pressure was maintained at 8 Torr during the process. The CVD durations of 1, 2 and 3 h were experienced.

During the synthesis process, in the first zone of CVD reactor, the sulfur powder vaporized and reacted with hydrogen gas to provide H₂S gas required for sulfurization reaction. In addition, H₂ gas is necessary to provide the reducing atmosphere in the CVD chamber. In the second region of the chamber, WO₃ nanoparticles are reduced by hydrogen and converted to WO₃₋ₓ and then reacted with H₂S gas to produce WS₂ at 850 °C. The WS₂/CNT proportions of 1:1, 1:3 and 3:1 are experienced. A schematic display for synthesis process is shown in figure 1.

#### 2.3. Preparation of Al-(WS₂/CNT) nanocomposite

Aluminum and hybrid WS₂/CNT powders were individually sonicated in acetone for 30 min. Then these were mixed and the final solution was sonicated for 2 h. The solution was then transferred to Planetary Ball Mill (stainless steel cup, balls whit10 mm diameter and ball to powder ratio (BPR) = 10:1) and milled for 5 h under
argon atmosphere at 250 rpm. The solution was then extracted from Ball Mill and dried in a vacuum oven at 80 °C. The resulting composite powder was transferred to a metal mold for hot pressing. Hot pressing process was operated under vacuum environment and at pressure, temperature, heating rate and pressing time of 150 MPa, 500 °C, 15 °C min⁻¹ and 40 min, respectively. Tablets with 10 mm height and 25 mm diameter was extracted from mold. Composition of samples is shown in table 1.

### 2.4. Characterization of WS₂/CNT hybrid material

The synthesized hybrid powder was characterized by x-ray diffraction (Philips, Cu Ka, λ = 1.54056 Å 2θ = 10–90 degrees), the output data were analyzed by the X-pert software to determine the type of constituent materials. Field Emission Scanning Electron Microscopy (FESEM, VEGA TESCAN-LMU, resolution = 5 nm) and Transmission Electron Microscopy (TEM, max voltage = 150 kV) were used for investigating the hybrid powder structure and morphology. Fourier-transform infrared spectroscopy (FTIR) spectra were measured by a Thermo Spectrometer. Almega Thermo Nicolet Dispersive Raman Spectrometer was used for recording the Raman spectra of hybrid material. The wavelength of the laser beam used was 532 nm and its power was 10 mW. Wavelength was measured up to 4000 cm⁻¹ and test duration was 5 s. The thermal behavior of the WS₂/CNT hybrid powder was also characterized by thermo-gravimetric analysis (TGA, Perkin Elmer) in the temperature range of 30 °C to 900 °C with a heating rate of 30 °C min⁻¹.

### 2.5. Characterization of hybrid nanocomposite

Archimedes technique was used to determine the density of samples according to the ASTM B962–17 standard [30]. In order to study the microstructure of the nanocomposite samples, Optical Microscopy (IM-X60) and Field Emission Scanning Electron Microscopy (FESEM) were used. After polishing the samples with 20-micron aluminum oxide powder, they were subjected to micro hardness test using Micro Vickers hardness according to the ASTM E384-99 standard [31]. The applied force was 50 grams and the dwell time was 10 s. Compressive test samples were cylindrical with a height to diameter ratio of 2. The compressive properties of the hybrid nanocomposites were measured according to ASTM E9-09 standard [32] using an Instron tensile machine with a strain rate of 0.4 mm min⁻¹ and a load of 15 N.
3. Results and discussion

3.1. Hybrid powder property

The CVD process was performed for 1, 2 and 3 h. After 1 h, as shown in the x-ray diffractogram (figure 2(a)) tungsten trioxide and tungsten metal are present. The higher intensity of the reduction reaction to sulfidation reaction is evident from this XRD pattern. Because of this, the pressure of the hydrogen gas was decreased and the reaction time was increased to 2 h, but some traces of tungsten trioxide still remain in the product while the tungsten is completely removed. Thus, with the same flow of gas, the time was increased up to 3 h, which eventually WO₃ is converted to WS₂ totally. In figure 2(a), the x-ray diffraction pattern were shown for all samples, indicating the WO₃ characteristic peak at $2\theta = 23^\circ$ is removed after 3 h. Also, WS₂ peaks located at $2\theta = 14.17^\circ$ (002), $33.16^\circ$ (011), and $39.21^\circ$ (013) are seen in XRD pattern [13, 15, 19, 21–26]. The XRD patterns for WS₂/CNT hybrid powder are shown in figure 2(b). The Peaks at $2\theta = 26^\circ$, $44.3^\circ$ correspond to CNT [13, 14]. As is clear from the graphs, by increasing the amount of CNT in the obtained hybrid particles, the intensity of CNT peak at $2\theta = 26^\circ$ increases dramatically. Crystallite size of WS₂ decreases by adding the CNT and the minimum crystallite size occurred in sample where the WS₂ and CNT weight ratio is 1:1.

![Figure 2. XRD patterns of (a) synthesized WS₂ (b) WS₂/CNT hybrid nanoparticles by various CNT content.](image)

| Table 2. Crystallite size of WS₂ in WS₂/CNT nanoparticle. |
|-----------------|-----------------|-----------------|-----------------|
| WS₂             | WS₂/CNT (3:1)   | WS₂/CNT (1:1)   | WS₂/CNT (1:3)   |
| Crystallite size (nm) | 27.1            | 14.8            | 13.8            | 14.9            |

Based on the literature [33–35], fullerene-like and nanotubes morphologies of tungsten disulfide, have three major differences in the Raman peaks compared to flake morphology. The peak at 152 cm⁻¹ and 2 to 6-digit shift in the E₂g₁ peak at the wavelength range of 348 cm⁻¹ and appearance of A₁g peak at 415 cm⁻¹ are three fundamental differences for determining the distinction between WS₂ flake with fullerene-like and tubes morphology of WS₂ [34, 35]. This shift in the peaks is due to the tension in the tubular structure wall. Figure 3 shows the Raman spectra of WS₂ and WS₂/CNT hybrid samples. The existing characteristic peaks and shift in the peaks for the obtained samples are shown in table 3. The appearance of a peak at 152 cm⁻¹, 6-digit shift in the E₂g₁ peak from 348 to 354 cm⁻¹ and 2-digit shift in the A₁g peak from 415 to 417 cm⁻¹ are indications for the formation of the tubular morphology of WS₂ in the obtained samples. The peak intensity ratio of A₁g and E₂g₁ peak in the hybrid specimens is higher than that of the pure sample, indicating a greater stress in the tubular structure and morphology of WS₂. A shift is also observed in carbon nanotube characteristic peaks, which shows the interaction of the structure of CNT and WS₂ and bond formation between them [14, 34–37].

Infrared spectroscopy is based on the absorption of radiation and the evaluation of the vibrational mutations of molecules and multi-atom ions. This method is useful for determining the chemical bonds on the surface. FTIR spectra of pure WS₂ and WS₂/CNT hybrid particle are shown in figure 4. The peaks at 470 cm⁻¹ is indication for elemental sulfur [38]. The peaks at 622 and 1092 cm⁻¹ correspond to W-S and S-S bonds,
respectively. The peaks at 1392.2 and 1632.4 cm$^{-1}$ represent hydroxyl groups and peaks at 2920.2 and 3433.8 cm$^{-1}$ are related to the O–H bond [39, 40]. Differences in spectra of hybrid particle compared to the pure sample are due to the presence of carbon nanotubes and their interactions at the surface. This difference leads to reflections in the range of 650 to 850 cm$^{-1}$, which is related to the C–S bond [41]. Of course, there are also C–S–S–C, H–C–S and C–S (780 cm$^{-1}$) bonds in this range [42]. There is a weak peak at 1445 cm$^{-1}$ that refers to multi-walled carbon nanotube [43]. According to these FTIR spectra, it can be easily proved that the interaction
between carbon nanotube and tungsten disulfide has successfully occurred, this observation is consistent with the results of the Raman spectroscopy results.

3.2. Hybrid powder morphology
The microstructural and morphological properties of WS₂ and WS₂/CNT hybrid nanostructure, were investigated using FESEM and TEM as shown in figure 5. According to figure 5(a), FESEM image of WS₂ nanoparticle, the morphology of WS₂ is tubular. Figure 5(b), represents TEM image of WS₂ nanotubes indicating they are wrapped around a single axis and exhibit continuous fractures in the inner wall. These findings are consistent with the findings of other researchers [20]. FESEM micrograph of WS₂/CNT hybrid powder is shown in figure 5(c). There are WS₂ nanotubes along with a nanoflake mass, as well as carbon nanotubes in the FESEM result. This indicates that the presence of carbon nanotubes during processing of WS₂ encourages producing other morphologies of WS₂ including fullerene-like and nanoflake morphologies. In figure 5(d), the presence of tungsten disulfide nanoparticles on CNT is clearly seen, which confirms the WS₂/CNT hybrid formation. The results of TEM and FESEM tests are in line with the findings of the Raman and FTIR characterization as mentioned in the previous section.

3.3. Hybrid powder thermal stability
The weight loss of WS₂ and WS₂/CNT hybrid sample are shown in figure 6. The weight loss of WS₂ (figure 6-black line) is less than 4% by 475 °C, indicating the high purity of this sample because in this stage, the moisture and organic matters with physical bond are removed. By starting WS₂ conversion to WO₃, the sample weight loss continues up to 580 °C, and the total weight loss in this stage is less than 10%. The green powder weight remains constant up to 900 °C. For CNT, the oxidation reaction starts at around 500 ± 20 °C and more than 99% of the sample weight is lost in the temperature range of 500–700 °C. The remaining black ash includes the oxide impurities as well [44–46]. In contrast, in the hybrid sample (figure 6-red line) the first degradation temperature due to the tungsten disulfide oxidation is about 495 °C, with less than 3% reduction in sample weight. This temperature is 15 °C higher than the WS₂ sample. The second degradation temperature that is related to carbon nanotube oxidation, starts at 620 °C. Its total weight loss is about 6% and its temperature is 100 °C higher than the starting temperature of degradation of carbon nanotube and 40 °C higher than the ending temperature of degradation of WS₂ sample. The specimen lost 30% of its total weight at 770 °C, and the weight is constant up to 900 °C. Similar results were reported by other researchers [37]. The TGA test shows thermal stability of WS₂/CNT hybrid powder is higher than CNT and WS₂ individually.
3.4. Microstructure of Al-(WS₂/CNT) hybrid nanocomposite

The FESEM micrograph of Al-(WS₂/CNT) mixed powders is shown in figure 7. According to this image, the distribution of WS₂ and CNT in Al powder is good and both reinforcements are absorbed on aluminum flakes. The reason is the similar morphology of aluminum powder and two reinforcements. Reducing the difference in the aspect ratio of the aluminum and reinforcing powders results in closer morphology of the powders and a better distribution. In the milling process, the ball act as a micro-roller and the soft aluminum particles are rolled and their morphology alters to flake [47]. Tungsten disulfide and carbon nanotube are one-dimensional nanostructures. Aluminum flake morphology is closer to the morphology of the reinforcing particles than spherical morphology (the initial morphology of aluminum powder) and thus their distribution is becoming better.

The microstructures of the samples are shown in figure 8. The grains in the samples are fine and it seems that the agglomeration has mostly occurred at the grain boundaries. Introducing of reinforcing particles to grain boundaries prevents grain movement and makes them finer. It is seen that with increasing the CNT content, the grains become finer but the thickness of the grain boundaries increases. The decrease in grain size with the addition of tungsten disulfide or carbon nanotube in the aluminum matrix has also been reported by other
researchers [48, 49]. This phenomenon indicates the ability of these particles to prevent grain boundary movement in the sintering process to reduce the grain size [48, 49]. The microstructures of all samples are similar. It seems that HNC0.5 sample has more uniform structure with better dispersion of WS$_2$-CNT reinforcements compared to others samples.

Figure 9, is the FESEM image of polished surface of hybrid specimen containing 50% carbon nanotubes. This image shows the presence of carbon nanotubes and tungsten disulfide alongside each other in a compressed structure. Remaining the primary structure of the reinforcement intact in the final structure is particularly important for the carbon nanotube. Because desirable properties of nanoparticles can be effective in composite, if the primary structure and size of the particles is maintained unchanged during the manufacturing process of the composite. Generally, with particle size less than 200 nm, an acceptable interface is formed between the matrix and the reinforcement, which will increase the mechanical properties. In addition, with the proper distribution of nanoparticles in the matrix due to the wide nanoparticle surface, the amount of interface in the structure will increase sharply, which will lead to better load transfer from the matrix to the reinforcement [50]. According to figure 9, morphology and the size of the reinforcements have remained in the primary form and there is perfect interface between aluminum matrix and reinforcements. Therefore, the production process used in this research, is suitable and improves the mechanical properties.
3.5. Mechanical properties of the hybrid nanocomposite

Density of nanocomposite has a direct effect on its mechanical properties. Density of hybrid nanocomposite was measured by the Archimedes method. The variations of relative density with carbon nanotube content are shown in Figure 10(a). As is clear from this image, the relative density of the hybrid nanocomposite samples is in the range of 99%–99.8% and the highest density is related to the HNC0.5 sample with the value of 99.8%. In general, compressing the powders containing nanoparticles is more difficult than compressing the pure powder of the base metal in micron range, and thus more pressure is needed than that of pure sample to achieve a high relative density. The reason is the vast surface area of the nanoparticles in the structure that results in an increased inter-particle friction. The cavities are created inside and between the grains during the hot-pressing process. Particle re-arrangement, local deformation, bulk deformation and difference between thermal expansion coefficient (TEC) of reinforcements and the matrix are four mechanisms that affect the compressibility [49]. Diffusion is an important mechanism in bonding the particles during the sintering process. As the result of this mechanism a better compressibility is expected. The diffusion process is more difficult in presence of the nanoparticles. By increasing the weight percentage of the nanoparticles and creating clusters and agglomerates, the inter-particle cavities are created which decreases the relative density. [51]. In contrast, some researchers have reported that the cavities between aluminum powder are filled by nanoparticles and because of their small size, they have negligible effect on the reduction of diffusion process. Therefore, the relative density increases in the nanocomposite [11, 48, 51]. For solid lubricator nanoparticles such as tungsten disulfide, relative density of nanocomposites enhances due to inter-particle lubrication and reduced friction coefficient between the particles [11, 48, 52]. In the present study, the addition of up to 1 wt% tungsten disulfide nanotubes to aluminum matrix increased the density up to 99%, which is consistent with the results of other researchers [11, 48]. The maximum relative density occurred in HNC0.5 sample where the WS₂ and CNT weight ratio is 1:1. The better distribution of hybrid particles in the sample and the proper adsorption of the hybrid particles on aluminum powders that was observed in section 2.3, can have a significant effect on its enhanced density. In addition, tungsten disulfide particles that present on carbon nanotubes surface, will reduce the friction between particles in the compression process and prevent the agglomeration of carbon nanotube particles [48].

The hardness of the hybrid samples was measured using a micro hardness tester. Variation of hybrid nanocomposites hardness with carbon nanotube content is shown in Figure 10(b). The hardness of the hybrid nanocomposites is between 82 to 92 micro Vickers, and has a maximum in HNC0.5 sample. Addition of
nanoparticles to the aluminum matrix generally increases the hardness of the nanocomposite. Various factors contribute to the hardening the nanocomposites, which include preventing of migration of the grain boundaries and dislocations that affect the strengthening mechanisms such as Orowan, Hall-Petch and dislocation density mechanisms. In fact, nanoparticles which are embedded inside the grains or at grain boundaries will affect the mechanisms associated with the load transfer from the matrix to the reinforcements. Uniform distribution of nanoparticles in the matrix reduces the inter-particle distance in the structure, which prevents the dislocation movement. The surface of the nanoparticles is very active so it creates a large surface area and motivates the formation of hard phases in the matrix such as aluminum carbide that may also be effective in enhancing the hardness of the samples [48, 49, 51]. Hardness behavior of the nanocomposites is similar to the relative density behavior mentioned above. The hardness of all hybrid specimens is higher than samples with 1 wt% CNT and 1 wt% WS₂, which suggests that hybridization has a positive effect on the hardness of the nanocomposite.

To investigate the mechanical properties of the nanocomposites, samples were subjected to compressive test. The compressive strength of the specimens is shown in figure 10(c). The behavior of the hybrid nanocomposites in compressive test is similar to their behavior in hardness and relative density evaluation. The compressive strength versus the carbon nanotube content has maximum value at equal proportions of reinforcements (WS₂/CNT 1:1). Nanoparticles can increase mechanical strength of the samples by at least four reasons. The first reason is difficulty in motion of the dislocations in presence of reinforcing nanoparticles due to the stress field created around them. The second reason is increase in dislocation density due to the presence of nanoparticles caused by the mismatch of the thermal expansion coefficients of the matrix and reinforcements or the creation of the Orowan rings. The effect of nanoparticles on grain size reduction and the locking of cracks by nanoparticles are other reasons. The interface between the reinforcement and matrix transfers the load from the matrix to the reinforcement and controls the strength of the nanocomposites. The non-uniform distribution of the nanoparticles can lead to the formation of agglomerates in the structure that severely affect the mechanical properties. Agglomerates create stress-focused areas in the structure, that in turn, they increase the cavities and accelerate separation in structure and crack formation [48, 49, 53]. The effect of the carbon nanotube on the mechanical properties of aluminum composites depends on three factors: distribution, volume fraction, and interfacial bonding between aluminum and carbon nanotubes [51]. Good dispersion of reinforcements, high relative density indicating very low porosity content of the structure of the specimens, impeding the crack growth, reducing the grain size and preventing dislocation movement are the effective factors in increasing the compressive strength of the hybrid nanocomposites. By increasing the load, these specimens converted to barrel form, eventually turned to a complete disk with no cracks on surface or side. It seems that the hybrid nanoparticle have a high potential in preventing crack growth in the nanocomposite.

3.6. The main affecting factors on strengthening of hybrid nanocomposite

As mentioned in section 3.5, WS₂/CNT hybrid nanoparticles enhanced the relative density. By increasing the relative density, porosity decreases and thus the strength enhances dramatically. So, the first effect is due to the increase in the density of the nanocomposites [54].

The second effect is the role of the hybrid nanoparticles in production and congestion of the dislocation. In matrix that is reinforced by tubular nanostructures, the dislocation congestion pileups behind reinforcing nanoparticles increases the strength according to Taylor’s equation [55]:

$$\sigma = \sigma_0 + \alpha M^* G b \rho^{1/2}$$

That $\sigma$, $\sigma_0$, $\alpha$, $M^*$, $G$, $b$, $\rho$ are stress, frictional stress, constant, Taylor factor (in polycrystalline materials equal to 3), shear modulus, Burgers vector, and dislocation density of aluminum respectively. According to this equation, by increasing the amount of the carbon nanotubes, the composite strength increases as well. However, in higher carbon nanotube contents, due to the formation of clusters and agglomerates this mechanism does not work. Lahiri et al [56, 57] confirmed this mechanism in aluminum matrix. In this study, thermal expansion coefficient for carbon nanotubes, tungsten sulfide and aluminum are equal to $2 \times 10^{-5} \text{K}^{-1}$, $14.8 \times 10^{-6} \text{K}^{-1}$, $24 \times 10^{-6} \text{K}^{-1}$ respectively [58, 59]. There is a significant difference between the thermal expansion coefficient of the reinforcements and matrix, which causes the thermal stress in the reinforcement interface area in matrix and around the reinforcement themselves. They prevent dislocation movement and dislocations accumulation around them.

The third reason is grain-boundary strengthening mechanism, according to the Hall-Petch equation [60, 61], nanoparticles located at grain and nanosized sub-grains boundaries inhibit sticking the grains together and forming larger grains during heating [62]. Hybrid reinforcing nanoparticles cover the whole surface of the aluminum powders and its presence at boundary between powders prevents the grain boundary movement. The pressure in the hot-pressing process as well as the residual stress in the powder due to milling process make new grains in the structure by nucleation in the nanosized range. Hybrid nanoparticles near the new nucleuses, prevent them from bounding together and thus controls grain growth.
4. Conclusion

A simple, safe and low-cost method for fabrication of the WS$_2$/CNT hybrid nanoparticles via CVD process was developed without using H$_2$S gas in which the WO$_3$ synthesis stage was removed from the processing steps. XRD, Raman and FTIR analyzes confirmed the successful fabrication of pure and homogenous WS$_2$/CNT hybrid nanoparticles. TGA analysis of the hybrid nanoparticles indicated the total weight loss of about 30% up to 900 °C. The thermal stability of the hybrid nanoparticles was more than tungsten disulfide and carbon nanotube. FESEM and TEM images revealed tubular structure for tungsten disulfide located on the carbon nanotube surface. The synthesized hybrid nanoparticles with various WS$_2$/CNT ratios in 1 wt% were added to aluminum matrix. OM and FESEM analyzes of hybrid nanocomposite samples clearly showed the good dispersion of hybrid nanoparticles in Aluminum matrix. The maximum relative density more than 99.5%, maximum hardness and highest compressive strength were obtained for the nanocomposite with 1:1 WS$_2$/CNT ratio. Hardness was reached to 99 micro Vickers. The value of the compressive strength represented more than 60% increase compared to pure aluminum. Orowan mechanism, preventing dislocation movement, hindering the crack growth and reducing the grain size are the main reasons for the enhancement of mechanical property of the obtained hybrid nanocomposites.

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