Microstructure and mechanical properties of zinc matrix composites reinforced with copper coated multiwall carbon nanotubes

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Abstract
Zinc alloy has been considered as a promising candidate for orthopedic implants due to its suitable degradation rate and good biocompatibility. However, its mechanical properties still have to be optimized. Metal matrix composites (MMC) are an effective way to improve the mechanical properties of zinc alloy. In this study, pure zinc as matrix, Cu-coated multiwall carbon nanotubes (MWCNTs) were used as reinforcement, and MWCNTs/Zn composites were successfully prepared by combining the use of electroless deposition (ED), spark plasma sintering (SPS), and hot-rolling techniques. The results show that MWCNTs are uniformly dispersed in the zinc matrix and a tight interface is formed between the MWCNTs and the zinc matrix. As the content of the MWCNTs increases, the mechanical properties of the MWCNTs/Zn composites gradually increase. The Cu-coated MWCNTs/Zn composites have higher mechanical properties than uncoated Cu. 3 vol% Cu-coated MWCNTs/Zn composite has a highest ultimate tensile strength of 281 MPa, but the elongation is only 4%. Load transfer effect and fine grain strengthening are two main strengthening mechanisms of MWCNTs/Zn composites. This research provides a new method for the design and preparation of MWCNTs/Zn composites.

1. Introduction
In recent years, research on biodegradable magnesium and iron alloys has been increasing [1–8]. This research has shown that the degradation rate of magnesium alloys is too fast or the degradation is not uniform, resulting in insufficient support or fixing ability. The degradation rate of iron alloys is relatively slow, and their degradation products can remain stable in the human body for a long time. Because the standard electrode potential of Zn (−0.763 V) is between Mg (−2.372 V) and Fe (−0.447 V) [9, 10], from the perspective of corrosion resistance, zinc is expected to show a suitable degradation rate. In addition, zinc participates in a large number of physiological responses of the human body, including cell development and growth, gene expression, the immune system and the nervous system, etc [10–12]. More importantly, zinc plays an important role in the growth and mineralization of bone tissue. Zinc inhibits osteoclastic bone resorption by inhibiting osteoclast-like cell formation from marrow cells [13]. Based on the above advantages, zinc alloys are expected to be a substitute for Mg and Fe matrix alloys in degradable implant materials. However, pure zinc has lower mechanical properties, and it may still corrode too quickly in the human body [8].

MMC is one of the feasible methods to improve the mechanical properties of pure zinc. The mechanical properties of the matrix are further improved by selecting a suitable reinforcement. MWCNTs are used as ideal reinforcements for composites due to their excellent properties, light weight, extremely high Young’s modulus, high tensile strength, and good thermal conductivity [14–16]. At present, MWCNTs have played a critical role in strengthening copper matrix, aluminum matrix, and magnesium matrix composites. Bohua Duan et al [17], reported effect of MWCNTs content on microstructure and properties of MWCNTs/Cu composites. The strength and plasticity of the 1 vol% composite are perfectly matched, when the tensile strength is 218 MPa, the
elongation reaches 38%. Baisong Guo et al. [18], reported MWCNTs/Al composites. The improvement of the mechanical properties of composites is based on the close bonding between MWCNTs and Al matrix, grain refinement, and uniform dispersion and integrity of MWCNTs. Li et al. [19], studied the microstructure and strengthening mechanism of MWCNTs/Mg composites, MWCNTs significantly refine the grains and enhance the strength of the matrix. The above research results provide a new choice for the strengthening method of Zn matrix composites.

Based on the above research results, in this study, MWCNTs will be introduced into the Zn matrix to improve the mechanical properties of pure Zn with a view to applying MWCNTs/Zn composites in bone tissue engineering. However, the real challenges for the MWCNTs/Zn composites are: (1) uniform dispersibility of MWCNTs in the Zn matrix. MWCNTs have a large specific surface area and high specific surface energy, therefore, they have a strong tendency to agglomerate. When preparing MWCNTs/Zn composites, the key step is to make the MWCNTs uniformly dispersed in the Zn matrix to prevent the MWCNTs from agglomerating in the matrix to form weak phases. Weak phases easily cause pores and cracks, especially when the MWCNTs are agglomerated at the grain boundaries. The grain boundary strength will decrease greatly, which is harmful to the improvement of the mechanical properties of Zn matrix composites. (2) Interfacial wettability of MWCNTs and the Zn Matrix. The non-wetting of MWCNTs with most metals results in low bonding strength with the matrix, which makes the reinforcing effect lower than the ideal performance index. Therefore, seeking a suitable preparation process and optimizing the interfacial structure of the MWCNTs with Zn matrix are the key to the development of high-performance MWCNTs/Zn composites. In this study, the method of ED is used to improve the dispersibility and interfacial wettability of MWCNTs.

2. Materials and experimental procedures

2.1. Raw materials

Multiwall carbon nanotubes (MWCNTs, purity greater than 98%, outer diameter 10–20 nm, length 10–30 μm, theoretical density of MWCNTs is 1.76 g cm⁻³, Chengdu Institute of Organic Chemistry, China Academy of Sciences). Pure zinc powder (purity 99.5%, average grain size 5 μm, Zhongnuo New Materials Technology Co. Ltd., Beijing).

2.2. Acid treatment and electroless deposition Cu experiment

Figure 1 showed the schematic description of method and process for preparing the MWCNTs/Zn composites. Firstly, the original MWCNTs were purified with HNO₃ (61 wt%) for 10 h. Subsequently, a H₂SO₄ (97 wt%)/HNO₃ mixed solution (3:1, v/v) was used for 3 h in an ultrasonic water bath (KQ-5200) for acid pretreatment (figure 1(a)). Secondly, the acidified MWCNTs were sensitized with a SnCl₂/HCl (35%) solution for 20 min and magnetically stirred for 20 min. Then the sensitized MWCNTs were activated with a PdCl₂/HCl solution for 20 min and magnetically stirred for 20 min (figure 1(b)). Finally, the Cu-coated layer was acquired on the surface of MWCNTs in a water bath (DF-101S), deposition time is 45 min, temperature and PH are 60 °C and 11–12, respectively (figure 1(c)), and the 1 mol/l NaOH solution is used to adjust the pH of the coating solution. The chemical composition of the coating solution is listed in table 1. The Cu-coated MWCNTs were dried at 70 °C for 15 h in a vacuum.

2.3. Mixing of composite powders and fabrication of MWCNTs/Zn composites

Pure Zn powders and MWCNTs with different content were mixed in a planetary ball mill (QM-3SP2) with ball to powder ratio is 10:1. In this paper, variable-speed ball milling (150 rpm for 3 h, 280 rpm for 1.5 h and 300 rpm for 0.5 h) was used, and alcohol was used as a process control agent (figure 1(d)). The composite powders were dried at 70 °C for 25 h in a vacuum. Subsequently, the composites were sintered by spark plasma sintering (SPS-625HF). Pure Zn was also sintered using the same process for reference. The sintering temperature and heating rate are 340 °C and 100 °C/min, respectively. The sintering pressure and holding time are 30 MPa and 8 min, respectively, and the sample size is Ø 60 mm × 5 mm (figure 1(e)). Because Zn powder is volatile, it must be protected by an inert atmosphere during the sintering process. In addition, Zn is close-packed hexagonal structural and brittleness, so aluminum sheet (6061) was used for encapsulation rolling. As shown in figure 1(f) the rolling direction of the aluminum sheet is open, and the other directions are closed. The sample was preheated to 380 °C for 30 min and hot-rolled from 5 mm to 1.5 mm. The total number of rolling cycles and deformation were 7 and 70%, respectively. After each rolling pass, the sample was annealed at 380 °C for 5 min (figure 1(g)).
2.4. Characterizations
All samples were cut to a size of 3 mm × 5 mm (rolling direction) by electric spark cutting. The samples were ground to 3000 grit and polished with W3.5 metallographic polishing suspensions, and etched for 4 s in Nitric alcohol solution (4 HNO₃:96 C₂H₆O). Then the metallographic observed by ICX41M (Ningbo Sunny Instruments Co., Ltd, Ningbo, China) optical microscope (OM). The dispersion degree of the MWCNTs/Zn composite powders, the microstructure and the fracture morphology of the MWCNTs/Zn composites were characterized the field emission scanning electron microscope (SEM, Supra 40). A transmission electron microscope (TEM, FEI Talos F 200) was used to observe the microstructure and interface of the MWCNTs/Zn composites at 200 KV. The interface elements were analyzed using an energy spectrometer (Super-X G2 EDS Detector). The degree of damage to the MWCNTs were characterized by Raman spectroscopy (LabRam ARAMIS), the test range wave number is 1200–2200 and the laser wavelength is 325. Analysis of C=O, C–O bonding by Fourier transform infrared spectroscopy (FT-IR, Nicolet IS 10). Taking the binding energy of carbonaceous C1s (284.6 eV) as a reference, the XPS spectra of MWCNTs was analyzed by Thermo ESCALAB 250XI through a monochromatic Al Kα x-ray source and an x-ray beam of about 1 mm. A universal testing machine (TSE 104B) was used to study the tensile properties of the material at a deformation rate of 0.5 mm/min at room temperature. A microhardness tester quantified the hardness of the material (HVS-1000) with a load of 50 gf and a dwell time of 10 s.

3. Results
3.1. Characterization of MWCNTs and MWCNTs/Zn composite powders
As shown in figure 2, TEM observed the morphological changes of the original, acid-treated and Cu-coated MWCNTs. In figure 2(a) the original MWCNTs are highly tangled. There are defects on the outer wall of the
original MWCNTs (as shown by the white arrows in the figure), and the inset shows the intertubular spacing is 0.34 nm of MWCNTs in figure 2(b). After the acid treatment, the dispersibility of the MWCNTs is improved (figure 2(d)), and the acidified MWCNTs have higher crystallinity (figure 2(d)). However, defects were
introduced at the ends of the MWCNTs (figure 2(d)), which were consistent with the conclusions of Weiwei Zhou et al [20]. The surface morphology of the Cu-coated MWCNTs is shown in figures 2(e), (f). The nano Cu-coated layer increases the interfacial wettability of MWCNTs and Zn matrix, which provides a tight interfacial bonding between the MWCNTs and Zn matrix.

The Raman spectrum of the original, acidified, Cu-coated MWCNTs is shown in figure 3(a). The peak at 1355 cm$^{-1}$ is the MWCNTs defect peak (D), and the peak at 1554 cm$^{-1}$ is the graphite peak (G) in the Raman spectrum. ID/IG is the ratio of the intensity of the defect peaks to the graphite peaks in MWCNTs [21]. This is indicative of the quality of the MWCNTs. The ID/IG ratio of the original MWCNTs is 0.66, and the ID/IG ratio of acidified CNTs is 0.74. This shows that the defects increased slightly after acidification. However, the ID/IG ratio of Cu-coated MWCNTs is 0.16, which greatly reduced when compared to the original MWCNTs defects. This result shows the integrity of MWCNTs is increased after Cu coating. During the deposition process, the structure of the MWCNTs is greatly restored due to the recovery of the sp2-bonded carbon lattice [22]. Dusan and Jie et al proved that the integrity of MWCNTs provides the ability for bone tissue repair and regeneration [23, 24]. FT-IR spectrum (figure 3(b)) shows that the O atoms on the surface of the MWCNTs and C atoms are chemically bonded after Cu coating, as verified by the XPS spectrum in figure 4.

The morphology of MWCNTs/Zn composite powders are showed in figure 5. The Cu-coated MWCNTs/Zn composite powders are showed in figures 5(a)–(e), and the uncoated MWCNTs/Zn composite powder is showed in figure 5(f). When the MWCNTs content is not more than 2 vol%, the MWCNTs are uniformly distributed in the spherical zinc powders (figures 5(a)–(d)). As shown in figures 5(e), (f), the aggregation will...
appear in composite powders when the MWCNTs content exceed 2 vol%, however, the phenomenon of agglomeration of uncoated MWCNTs is more serious.

### 3.2. Microstructure and mechanical properties of MWCNTs/Zn composites

Figure 6 shows the SEM morphology Cu-coated MWCNTs/Zn composites after rolling. As can be seen from figure 6, the MWCNTs are uniformly dispersed in the Zn matrix (figures 6(a)–(e)). However, when the MWCNTs content is greater than 1.5%, MWCNTs agglomerate and form a large entangled network (figures 6(c)–(f)). Figure 6(f) is an enlarged drawing of the yellow rectangular box in figure 6(e), and the red arrow indicates the agglomerated morphology of MWCNTs in the Zn matrix.

Figure 7 shows that the ultimate tensile strength and microhardness of the hot-rolled composites gradually increase with the addition of MWCNTs. When the content of the MWCNTs is less than 1.5 vol%, due to less MWCNTs content, the ultimate tensile strength and microhardness of the composites increase relatively slowly. However, when the content of MWCNTs exceeds 1.5 vol%, the ultimate tensile strength and microhardness of the composite materials increase rapidly. When the content of MWCNTs exceeds 2 vol%, because of the serious agglomeration phenomenon of MWCNTs, the ultimate tensile strength and microhardness of the composites increase slowly. Finally, the 3 vol% Cu-coated MWCNTs/Zn composite exhibits excellent mechanical properties, ultimate tensile strength of 281 MPa, and microhardness of 89 HV (compared to the pure Zn an improvement of 127%, 37% respectively), compared to the 3 vol% uncoated MWCNTs/Zn composite increases by 25% and 5%, respectively, but elongation is only 4% (figure 8). As Cu-coated MWCNTs increased the interfacial wettability with the Zn matrix, the strength and microhardness are significantly improved.

### 4. Discussion

#### 4.1. Distribution of O atoms and its effect on mechanical properties of MWCNTs/Zn composites

Many researches have shown that a close interface can be established between MWCNTs and matrix through the surface of MWCNTs modified by various oxygen-containing functional groups such as carboxyl (–COOH), hydroxyl (–OH), and atomic oxygen (–O) [22, 25, 26]. They also found O atoms have a beneficial effect on the interface strength at the interface between the MWCNTs and the metal [22, 27–29]. However, the function and chemical structure of O atoms at the atomic level are still not really proved [30, 31].

Figure 9 shows the SEM image of 3 vol% Cu-coated MWCNTs/Zn composite and the element maps of Zn, C, O, and Cu. The elemental maps of O atoms and C atoms are homologous, indicating that the distribution of O atoms does not exhibit great variety during ED and SPS process, O atoms still exists in the sintering composites [25]. Oxygen is formed on the surface of MWCNTs during the pretreatment process (figure 1(b)), and C–O and C=O are chemically bonded during ED (figure 4). Therefore, we believe that an oxygen-containing interface is formed between the MWCNTs and Zn matrix.
Figure 6. SEM morphology of Cu-coated MWCNTs/Zn composites. (a) 0.5 vol% Cu-coated MWCNTs/Zn composite, (b) 1 vol% Cu-coated MWCNTs/Zn composite, (c) 1.5 vol% Cu-coated MWCNTs/Zn composite (d) 2 vol% Cu-coated MWCNTs/Zn composite, (e) 3 vol% Cu-coated MWCNTs/Zn composite. (f) Yellow rectangular box local enlarged drawing in (e).

Figure 7. (a) Tensile strength of MWCNTs/Zn composites, (b) Microhardness of MWCNTs/Zn composites (the percentage of black indicates the increase of different MWCNTs content compared to pure Zn after hot-rolling, the percentage of red indicates the increase of Cu-coated MWCNTs compared to uncoated MWCNTs after hot-rolling).
TEM image (figure 10(a)) and the homologous EDX line scan (matrix Zn-A, interface-M and MWCNTs-B) results (figure 10(b)) of an assigned region in (a) of 3 vol% Cu-coated MWCNTs/Zn composite are showed. Clearly, there are a few O atoms in the Zn matrix. Furthermore, the O atoms are mainly located near or on the MWCNTs. In addition, the clear and tight interface is confirmed between the MWCNTs and Zn by HRTEM images (figures 10(c) and 11(d)). The Zn–O bond formation is confirmed by the FFT pattern (figures 10(f) and 11(f)) and selected area SAED patterns (figure 11(c)) in figure 11(b). ZnO with a hexagonal wurtzite structure (figure 10(f)) and a relatively rare sodium chloride octahedral structure ZnO (figure 11(f)) are formed at the Cu-coated MWCNTs/Zn interface. Then, it can be determined that the Cu-coated MWCNTs/Zn interface consists of Cu, Zn–O bond and a few O atoms, the formation of oxygen-mediated C–O–Zn bonding [32] plays an important role in the close combination of the matrix Zn and the MWCNTs. Therefore, it is necessary to explore its effect on the properties of the Cu-coated MWCNTs/Zn composites. Coleman established a model of the interface area related to the strength ($\sigma_i$) of MWCNTs composites [33], as shown in the following equation

$$\sigma_i = \sigma_m + V_f \left( 1 + \frac{2h}{d_{od}} \right) \left[ \frac{\sigma_i}{d_{od}} - \left( 1 + \frac{2h}{d_{od}} \right) \sigma_m \right]$$

(1)

Where $h$ is the thickness of the interface region, $d_{od}$ is the outer diameter of MWCNTs, $\lambda$ is the average length of MWCNTs, $V_f$ are the volume fraction of the MWCNTs, $\sigma_m$ is the yield strength of the matrix, and $\sigma_i$ is the shear
strength of the interface. Though the shear strength and interface thickness of this study cannot be confidently quantified, we can still draw the conclusion that according to the equation (1): the oxygen-containing interface is beneficial to the mechanical properties of the Cu-coated MWCNTs/Zn composites [22].
4.2. Effect of load transfer effect on mechanical properties of MWCNTs/Zn composites

The tight interface between the Zn matrix and MWCNTs is based on a powerful bridging function, which generated during ED process and increased during the SPS and hot-rolled processes. This promotes the interface shear strength and plastic deformation to form a good basis for load transfer efficiency [27, 34].

The fracture morphology of pure Zn shows toughness characteristics in figure 12(a). The coarse and tough dimples are elongated in the direction of hot rolling (figure 12(b)) and further determines the presence of plastic deformation and the outstanding fracture toughness. It can be seen that there are partial crystalline fractures of the fracture morphology of 3 vol% Cu-coated MWCNTs/Zn composite in figure 12(c). Figure 12(d) shows the embed and pull out of MWCNTs in the matrix. This obvious load transfer can be confirmed by observing the pull-out fracture and bridging of the MWCNTs at the fracture.

As shown in figure 13(a), MWCNTs are aligned along the hot rolling direction due to the plastic flow of the zinc matrix, which is conducive to fully exerting the longitudinal bearing capacity of the MWCNTs and helps to generate and store dislocations in the case of cracks [35]. Dislocations movement and diffusion (indicated by ‘T’) resulted in high density dislocations in the MWCNTs/Zn interface region (figure 11(e)). In addition, in figures 13(b), (c), some defects can be observed at the outer walls and ends of the MWCNTs, this is because the solidification process (such as SPS and hot-rolled) slightly affects the formation of defects.

4.3. Effect of grain size on mechanical properties of the MWCNTs/Zn composites

The metallographic images of pure Zn and Cu-coated MWCNTs/Zn composites are showed in figure 14. The grain size of pure Zn and Cu-coated MWCNTs/Zn composites are showed in figure 15, and by the intercept method to determine [36]. Evidently, the grain of the composites gradually decreases with the increase of the MWCNTs content, and the grains are stretched along the rolling direction. During the sintering process, the Zener pinning effect effectively inhibited the growth of Zn matrix grains. The grain size of the zinc matrix is calculated by

\[ D_m = \frac{c \times d_{od}}{V_f} \]  

Where \( d_{od} \) is the outer diameter of MWCNTs, \( V_f \)are the volume fraction of the MWCNTs, and \( c \) is a constant. In this paper, \( c \) and \( d_{od} \) are constant, so the average grain size \( D_m \) of the Zn matrix depends on the \( V_f \). When the MWCNTs content is less than 1.5%, the grain size of the Zn matrix can be calculated by formula (2). However, when the content of MWCNTs exceeds 1.5%, because of the agglomeration of MWCNTs (figures 6(c)–(f)), the \( D_m \) of the Zn matrix was calculated by the modified equation [22].
Figure 13. TEM morphology of the Cu-coated MWCNTs/Zn composites. (a) TEM image of 3 vol% Cu-coated MWCNTs/Zn composite. (b), (c) Local enlarged drawing in (a). (The white arrows indicate defects, the red arrows indicate the MWCNTs, RD and TD indicate hot-rolled and the transverse direction, respectively.)

Figure 14. Metallographic images of pure Zn and Cu-coated MWCNTs/Zn composites. (a) Pure zinc. (b) 0.5 vol% Cu-coated MWCNTs/Zn composite. (c) 1 vol% Cu-coated MWCNTs/Zn composite. (d) 1.5 vol% Cu-coated MWCNTs/Zn composite. (e) 2 vol% Cu-coated MWCNTs/Zn composite. (f) 3 vol% Cu-coated MWCNTs/Zn composite. (RD and TD indicate hot-rolled and transverse direction, respectively.)

Figure 15. Grain size of pure Zn and Cu-coated MWCNTs/Zn composites.
Due to the MWCNTs agglomeration, where \( d_c \) is the critical diameter of MWCNTs. With the increase of MWCNTs content, the agglomeration phenomenon becomes more and more obvious, and the agglomeration range expands (figures 6(c)–(f)), which makes \( d_c \) gradually increase. Therefore, the decline rate of the \( D_m \) gradually decreases under the collective effect of the \( d_c \) and the \( V_f \). The results show that the uniform distribution of MWCNTs in the matrix is the main factor to improve the mechanical properties of MWCNTs/Zn composites. In addition, when the content of MWCNTs is greater than 1.5%, the strength of the composite material rises rapidly, which also shows that fine grain strengthening is not the only strengthening method of MWCNTs/Zn composites.

In summary, the interfacial oxygen atoms have a beneficial effect on the bridge between MWCNTs and the metal matrix. The formation of oxygen-mediated C–O–Zn bonding makes Zn and MWCNTs more closely bound together. Based on the formation of such a tight interface, the strength of the MWCNTs/Zn composites is enhanced because of the ability of the MWCNTs to transfer the matrix load. In addition, the grain is significantly refined with increasing MWCNTs content, and the fine grain strengthening also contributes to the strength of the MWCNTs/Zn composites. Therefore, the strengthening method of MWCNTs/Zn composites can be summarized as: load transfer effect, fine grain strengthening. And the load transfer effect plays a dominant role, and the pull-out and embedding of MWCNTs at the fractures have proved a significant load transfer efficiency.

5. Conclusions

A new MWCNTs/Zn composites are synthesized by improving the agglomeration of the MWCNTs through combining use of the ED and the SPS methods. The main conclusions are as follows:

1. The strength of MWCNTs/Zn composites increased with the increase of MWCNTs content. When MWCNTs content was 3vol%, tensile strength reached 281 MPa, which was 127% higher than that of pure zinc.

2. Cu coating obtained by ED method improved the dispersibility and reduce the aggregation of MWCNTs in MWCNTs/Zn composites. At the same time, the C–O–Zn bonding was formed at the interface between the matrix and the reinforcement, which made the bond between MWCNTs and the Zn matrix closer.

3. The strengthening mechanism of MWCNTs/Zn composites mainly includes the load transfer effect and fine grain strengthening effect of MWCNTs.

Conflicts of interest

There are no conflicts to declare.

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