

Article

Zinc Matrix Composites Reinforced with Partially Unzipped Carbon Nanotubes as Biodegradable Implant Materials

Mei Fan ^{1,2}, Fei Zhao ^{1,2,*}, Yuan Liu ^{1,2}, Sheng Yin ^{1,2}, Shanshan Peng ³ and Zongkui Zhang ^{3,*}

¹ College of Materials and Metallurgy, Guizhou University, Guiyang 550025, China

² Key Laboratory for Materials Structure and Strength of Guizhou Province, Guiyang 550025, China

³ Hospital of Guizhou University, Guiyang 550025, China

* Correspondence: fzhao@gzu.edu.cn (F.Z.); zkzhang@gzu.edu.cn (Z.Z.)

Abstract: The activity of zinc is between that of magnesium and iron, and it has a suitable degradation rate and good biocompatibility. It has been regarded as a very promising biodegradable metal material for biomedicine. However, the insufficient mechanical properties of pure Zn limit its practical application in the field of orthopedic implants. In this paper, partially unzipped carbon nanotubes (PUCNTs) obtained by meridionally cutting multi-walled carbon nanotubes (MWCNTs) were used as reinforcements and combined with spark plasma sintering to prepare partially unzipped carbon nanotube reinforced Zn matrix composites. The effects of PUCNT addition on the microstructure and the mechanical properties of Zn matrix composites were investigated. The microstructure analysis showed the good interface bonding between PUCNTs and the Zn matrix. Additionally, the strength of PUCNTs/Zn composites showed a trend of increasing first and then decreasing with the PUCNT content increases. When the PUCNT content was 0.2 wt%, the tensile strength and yield strength of composites were about 78.4% and 64.4% higher than that of pure Zn, respectively, while maintaining a high elongation (62.6%).

Keywords: partially unzipped carbon nanotubes; mechanical properties; zinc matrix composites



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1. Introduction

Research results in recent years have shown that zinc matrix materials are a potentially degradable biomedical material [1–3]. Zinc is the second most abundant micronutrient in the human body. In addition to participating in the synthesis of hundreds of enzymes and cellular proteins, it is also very important for biological functions such as gene expression, apoptosis regulation, and DNA and RNA synthesis [2,4]. Additionally, the in vivo results show that the corrosion rate of pure zinc ranged in 10–50 µm/year and that it progressively increased during six months, thus ensuring timely degradation of the implant [5]. At the same time, the zinc ions generated by the degradation of zinc in the human body do not cause accumulation and are excreted through urine and feces, and they have good biocompatibility [1,6]. Therefore, zinc matrix materials are expected to be the next generation of biodegradable orthopedic implant materials. However, pure zinc has poor strength and plasticity and cannot meet the mechanical property requirements of biodegradable orthopedic implant materials, thus limiting its further clinical application [7]. Therefore, various zinc alloys, such as Zn-Mg [3], Zn-Ge [8], Zn-3Cu-Mg [9], Zn-Li [10], and Zn-Zr [11], have been investigated and achieved substantial advances in terms of their mechanical properties. Nonetheless, the tensile strength and plasticity of most existing zinc alloys are insufficient for orthopedic implant materials. Therefore, there is an urgent need to develop more biodegradable zinc-based materials with better mechanical properties.

Compounding is an effective way to improve the mechanical properties of metal materials. Many reinforcing materials, such as hydroxyapatite (HA) [12], tungsten carbide (WC) [13], graphene nanoribbons (GNRs) [14] and carbon nanotubes (CNTs) [15], have

been used to enhance the mechanical properties of metallic materials. It is worth noting that carbon nanotubes (CNTs) are regarded as the most ideal one-dimensional nanoscale enhancing materials due to their excellent mechanical, thermal and electrical properties [16]. However, the performance of CNTs/metal matrix composites (CNTs/MMCs) is often not as expected due to the agglomeration of CNTs and poor interfacial bonding with the metal matrix [17]. Therefore, researchers have developed techniques such as flake powder metallurgy [18], high-energy ball milling [19], and electroless plating [20] to improve the dispersion of CNTs in the matrix and enhance the interfacial adhesion between CNTs and MMCs. However, in addition to these two issues, load transfer is also limited by the low available interfacial area (AIA) of CNTs in the matrix [21].

Recent studies have shown that the preparation of partially unzipped carbon nanotubes (PUCNTs) with graphene on the surface while retaining the original tubular structure on the inner wall by oxidative unzipping methods can solve the problem of low AIA of carbon nanotubes [22]. Additionally, there is a strong interaction between the outer graphene layer and inner-layer CNTs of PUCNTs, and the hydrophilic functional groups such as hydroxyl (–OH) and carboxyl (–COOH) on the surface of PUCNTs can improve the interfacial wettability between PUCNTs and the metal matrix [23,24]. This makes PUCNTs have more advantages than CNTs, making them ideal reinforcements for the metal matrix. Therefore, in this paper, partially unzipped carbon nanotube reinforced Zn matrix composites were prepared by the spark plasma sintering (SPS) process. The effect of the addition of PUCNTs on the microstructure and mechanical properties of the composites was studied, and the strengthening mechanism of the PUCNTs/Zn composites was discussed in depth.

2. Materials and Methods

2.1. Raw Materials

The pure zinc powder used in the experiment was purchased from Beijing Zhongnuo New Material Technology Co., Ltd. (Beijing, China), and the purity and average particle size were 99.5% and 5 μm , respectively. Multi-walled Carbon nanotubes (MWCNTs) were purchased from Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences (Chengdu, China), with a purity of >98%, an outer diameter of 10–20 nm, a length of 10–30 μm , and a theoretical density of 1.76 g/cm³.

2.2. Preparation of PUCNTs

First, 1 g of raw MWCNTs was weighed and mechanically stirred in the mixed solution of concentrated H₂SO₄ and H₃PO₄ for 1 h at room temperature. Secondly, 2 g KMnO₄ was slowly added to the MWCNTs mixed solution and oxidized at 65 °C for 1 h. After the reaction, use deionized water for washing and centrifugation, and repeat the washing and centrifugation until the pH value is neutral. Then, freeze-dry for 48 h to obtain PUCNT powder.

2.3. Preparation of Composites

Pure zinc powder and PUCNTs powder (0.1, 0.2, 0.3 and 0.5 wt%, respectively) were mixed in a planetary ball mill (QM-3SP2, Nanjing, China), and a certain amount of ethanol was added as a process control agent. The ball-to-powder ratio is 5:1, the total ball milling time is 5 h, and the ball milling speed is 300 rpm/min. During the powder mixing period, stop rotating after every 60 min of mixing, and then continue ball milling and mixing in the opposite direction for 60 min after 15 min, and the cycle is repeated. PUCNTs/Zn composite powder was obtained by vacuum drying (80 °C) for 24 h after ball milling. The spark plasma sintering (SPS-625HF) was conducted at 340 °C with a heating rate of 100 °C/min and a holding time of 8 min under an axial pressure of 30 MPa to obtain cylindrical materials with a sample size of $\Phi 60\text{ mm} \times 8\text{ mm}$. Pure zinc prepared using the same process was used as a control. In addition, zinc is a brittle material with close packed hexagonal crystal structure and few slip systems. Direct hot rolling can easily cause specimen cracking. Therefore, in this paper, the aluminum plate (6061) processing die is

used for cladding rolling. Rolling process: the sample was kept at 380 °C for 0.5 h and hot-rolled from 8 mm to the final thickness of 2 mm. The deformation amount was 15% each time. After each pass, the sample was annealed at 380 °C for 5 min.

2.4. Microstructure Characterization

The raw MWCNTs and PUCNTs were characterized and analyzed by X-ray diffraction with a scanning range of 5–80° and a scanning speed of 3°/min. The surface elements and chemical bond compositions of raw MWCNT and PUCNT samples were analyzed by X-ray photoelectron spectra (XPS, Scientific K-Alpha, PA, USA). The structural changes of raw MWCNTs and PUCNTs were determined using a Raman spectroscopy (LabRam HR Evolution, Bruker, Germany, laser wavelength of 532 nm). A high-resolution field emission scanning electron microscope (FESEM, Zeiss Supra 40, Oberkochen, Germany) with its own EDS system was used to observe the fracture morphology of the samples. The microstructure and interfacial bonding of the samples were investigated using transmission electron microscopy (TEM, FEI Talos F200X, Hillsboro, OR, USA).

2.5. Mechanical Property Test

The tensile properties were tested using a universal mechanical testing machine (TSE-104B) at room temperature with a tensile speed of 1 mm/min. The standard length of the tensile specimen is 65 mm, the length of the parallel end is 15 mm, the width is 8 mm, and the thickness is 2 mm.

3. Results and Discussions

3.1. Characterization of PUCNTs and PUCNTs/Zn Powders

The unzipping process of MWCNTs was investigated in detail using TEM. It can be seen from Figure 1a that the raw MWCNTs have a tubular structure with a smooth surface. After oxidative unzipping, it can be observed that the outer wall of MWCNTs has been cut meridionally to form some graphene sheet structures, while the inner wall has a hollow structure of nanotubes (Figure 1b).

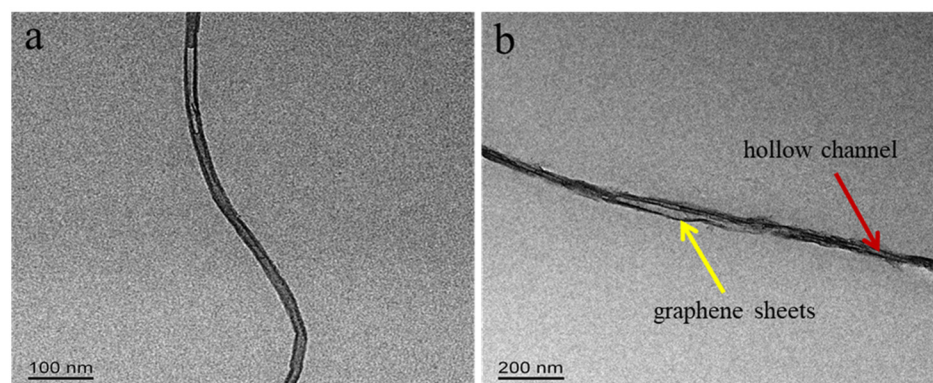


Figure 1. TEM images of (a) raw MWCNTs and (b) PUCNTs.

Figure 2a shows the XRD patterns of raw MWCNTs and PUCNTs. It can be intuitively seen that the structure of MWCNTs has changed. The raw MWCNTs have a strong diffraction peak at $2\theta = 26^\circ$, which is the diffraction peak of the (002) crystal plane of the graphene sheets in the MWCNTs, and the corresponding crystal plane spacing is 0.34 nm. In addition to a main diffraction peak at 25.8° , the PUCNTs obtained by oxidation unzipping showed a new diffraction peak at $2\theta = 10.8^\circ$, and the corresponding crystal plane spacing is 0.81 nm. In fact, the oxygen functional groups produced in the oxidation unzipping process can intercalate the graphene layers of MWCNTs, which increases the layer spacing of PUCNTs. Meanwhile, the XRD patterns of PUCNTs are basically consistent with those of unzipping carbon nanotubes reported in the literature [25], indicating that raw MWCNTs have been successfully meridionally cut into PUCNTs, in which graphene and CNTs coexist.

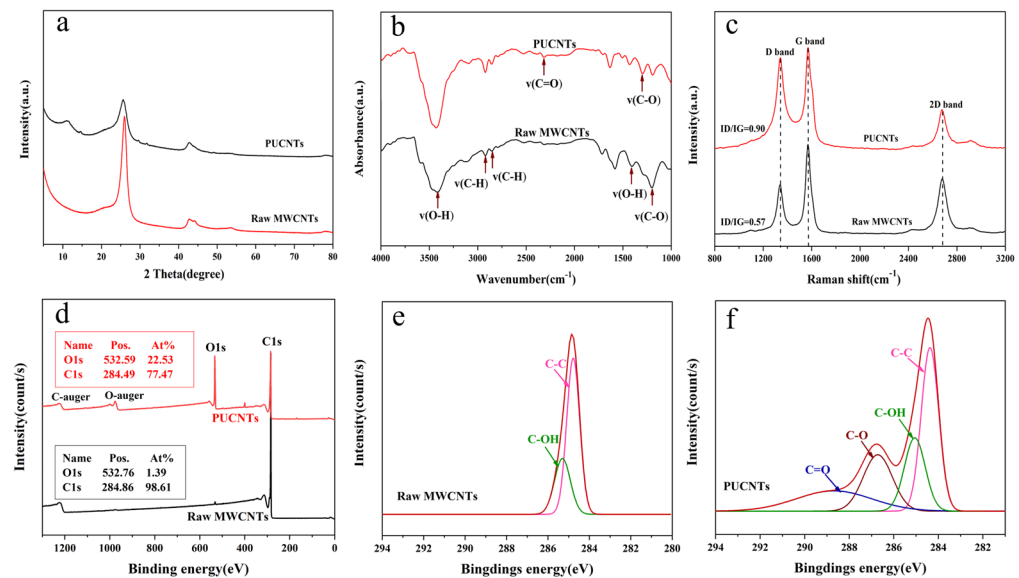


Figure 2. (a) XRD patterns of raw MWCNTs and PUCNTs. (b) FTIR spectra of raw MWCNTs and PUCNTs. (c) Raman spectra of raw MWCNTs and PUCNTs. (d) XPS measurement spectra of raw MWCNTs and PUCNTs. (e) High-resolution scans of the C1s region of raw MWCNTs and (f) PUCNTs.

The surface functional group types of PUCNTs and raw MWCNTs were analyzed by Fourier transform infrared spectroscopy (Figure 2b). The results show that there are mainly O–H ($\sim 3440\text{ cm}^{-1}$) stretching vibration absorption peaks, O–H ($\sim 1405\text{ cm}^{-1}$) deformation vibration absorption peaks, and C–H ($\sim 2920\text{ cm}^{-1}$ and 2854 cm^{-1}) stretching vibration absorption peaks in the infrared spectrum of pristine MWCNTs, as well as peak and C–O–C ($\sim 1192\text{ cm}^{-1}$) asymmetric stretching vibration absorption peaks. In the infrared spectrum of PUCNTs obtained by chemical unzipping, in addition to the increase in the intensity of the absorption peaks of the above oxygen-containing functional groups, two new absorption peaks of oxygen-containing functional groups also appear, which are located at the stretching vibration absorption peak of 2275 cm^{-1} and The C–O–H in-plane stretching vibration absorption peak at 1276 cm^{-1} indicates that the surface of PUCNTs obtained by oxidative unzipping contains a large number of hydrophilic functional groups [26].

The Raman spectra of raw MWCNTs and PUCNTs are shown in Figure 2c. There are three main characteristic peaks in the spectra of MWCNTs and PUCNTs, which are the 2D peak at 2675 cm^{-1} , the G peak at 1569 cm^{-1} and the D peak at 1340 cm^{-1} , respectively. The 2D peak is the second-order Raman scattering peak, which has a strong signal in the complete structure [27]. The surface defect level of a sample can be characterized by the Raman intensity ratio (ID/IG). The ID/IG value of raw MWCNTs was 0.57, and the ID/IG value of PUCNTs obtained by oxidative unzipping was 0.90. Compared with raw MWCNTs, the ID/IG value of PUCNTs was significantly increased by 58%, indicating that the chemical unzipping process significantly increased the number of defects in the structure of MWCNTs. Meanwhile, the 2D peak intensity decreased significantly after oxidative unzipping, which indicated that the multi-layer graphitic structure of CNTs was gradually destroyed [28]. Acik et al. [29] found that the ID/IG value increased from 0.8 to 1.34 during the unzipping of MWCNTs, and the increase in this value was largely dependent on the oxidation time and temperature.

The chemical states and oxygen-containing functional groups of raw MWCNTs and PUCNTs were analyzed according to XPS spectra. Figure 2d shows that the raw MWCNTs are composed of 1.39 at% oxygen and 98.61 at% carbon, while the oxygen content in the PUCNTs obtained by oxidative unzipping is greatly increased to 22.53 at%, indicating that the oxidative unzipping process introduces a large number of oxygen-containing functional

groups on the surface of PUCNTs. This was demonstrated by deconvoluting the peaks from the corresponding XPS spectra. There are four distinct peaks in the C1s spectrum of PUCNTs (Figure 2f), which are the C–C peak at 284.4 eV, the C–O–H peak at 285.1 eV, the C–O–C peak at 286.7 eV, and the C=O peak at 288.7 eV. The analysis results of XRD, Raman spectroscopy, infrared spectroscopy and XPS spectroscopy show that KMnO_4 easily modified the surface of CNTs to form defects and oxygen-containing functional groups. The oxygen-containing functional groups can improve the dispersibility of PUCNTs in ethanol, thereby obtaining uniformly dispersed PUCNTs/MMCs powders [30].

The SEM image of the ball-milled dispersed PUCNTs/Zn mixed powder is shown in Figure 3. It can be seen that some PUCNTs are embedded in the zinc particles, and some are coated on the surface of the zinc particles. When the content of PUCNTs was less than 0.3 wt% (Figure 3a,b), the PUCNTs were uniformly dispersed on the surface of the zinc particles. However, due to the flexibility and strong van der Waals force of PUCNTs, when the content of PUCNTs is too high, the PUCNTs in the composite powder appear to be entangled and agglomerated.

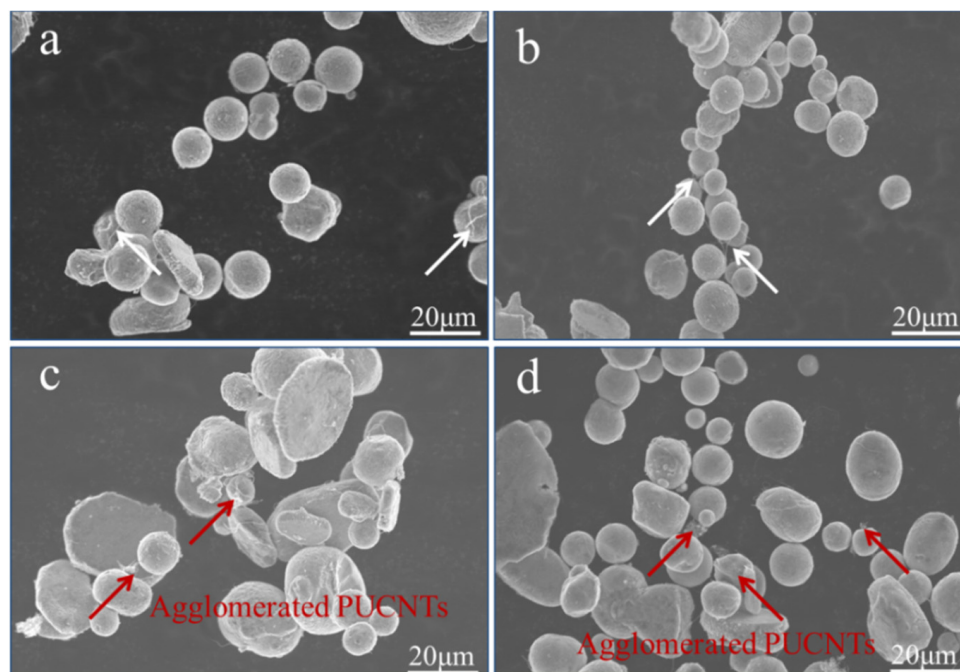


Figure 3. SEM morphology of (a) 0.1 PUCNTs/Zn, (b) 0.2 PUCNTs/Zn, (c) 0.3 PUCNTs/Zn, and (d) 0.5 PUCNTs/Zn powders.

3.2. Interface Structure of PUCNTs/Zn Composites

Figure 4 shows the TEM analysis of PUCNTs/Zn composites. As shown Figure 4a, it can be seen that the PUCNTs reinforcements are uniformly distributed in the composites. Under high magnification, the PUCNTs were observed to be in close contact with the Zn matrix and no obvious physical gap, indicating a good interfacial bonding between Zn matrix and the reinforcement (Figure 4b). Graphene sheets and a large number of oxygen-containing functional groups present on the surface of PUCNTs after oxidative unzipping, which can not only increase the interface contact area between the matrix and reinforcement, but also improve the wettability between the Zn matrix and PUCNTs [23,24]. Figure 4d shows the inverse fast Fourier-transform (IFFT) images of the black box in Figure 4b. As shown, dislocations (T-shaped symbols) near the interface can be observed. During the fabrication of the composites, due to the mismatch of the coefficient of thermal expansion (CTE) between the PUCNTs and Zn matrix, thermally mismatched residual stress will be generated near the interface, resulting in the formation of misfit dislocations, which help to promote the interface bonding [31]. The load transfer ability from the Zn matrix to

the PUCNTs was improved, thereby significantly improving the mechanical properties of the composites.

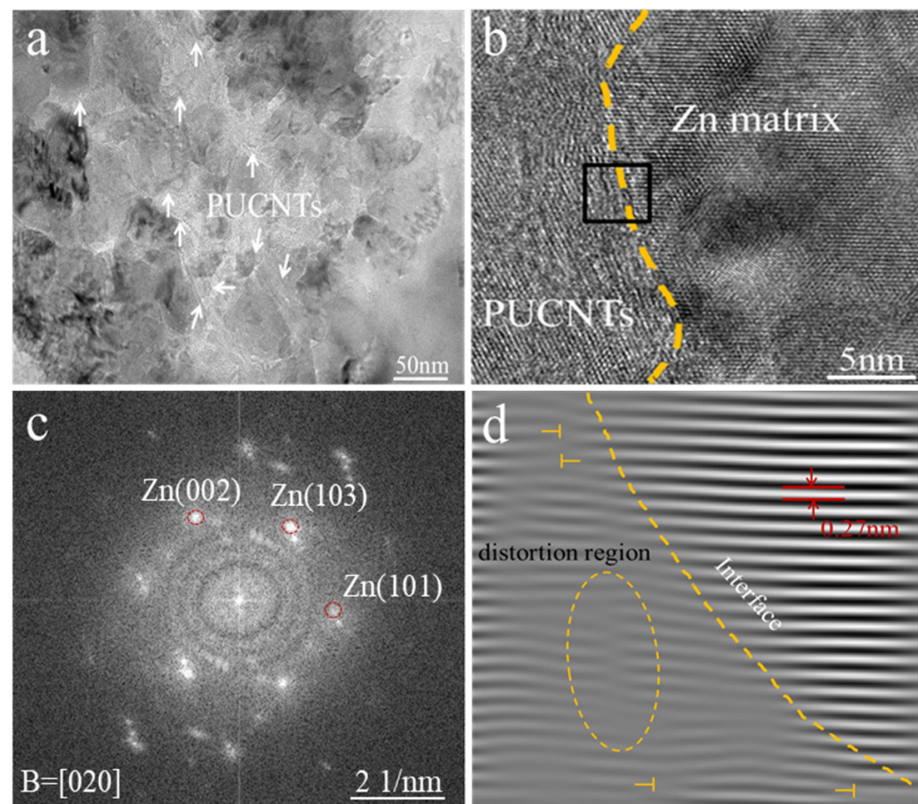


Figure 4. (a) TEM image of the PUCNTs/Zn composites. (b) The interfacial relationship diagram of Zn and PUCNTs. (c,d) The FFT and IFFT images of the black selected area in (b), respectively.

3.3. Mechanical Properties of PUCNTs/Zn Composites

Figure 5 shows the stress–strain curves and tensile properties of pure Zn and PUCNTs/Zn composites. It can be seen from Figure 5a that pure Zn exhibits a higher elongation (157.6%) at room temperature, which may be due to the occurrence of dynamic recrystallization. After adding PUCNTs, the tensile strength of the composite showed a trend of increasing first and then decreasing, while the elongation decreased rapidly. When the content of PUCNTs is 0.1 wt%, the tensile strength of the composite reaches 185.6 MPa, which is 57.3% higher than that of pure zinc without reinforcement. When the content of PUCNTs is 0.2 wt%, the tensile strength and yield strength of the composites both reach their maximum values, which are 210.5 and 169.7 MPa, respectively, which are 78.4% and 64.4% higher than that of pure zinc (118 MPa, 103.2 MPa), respectively, while the elongation (62.6%) remained at a higher level. However, the tensile strength of the composites began to decrease when the PUCNTs continued to increase, which may be due to the agglomeration of PUCNTs in the zinc matrix to form a weak phase (Figure 3c,d), which is prone to microcracks during the mechanical response process, leading to premature fracture of the composites. Therefore, the uniform distribution of nano reinforcements in the matrix is one of the key points to improve the mechanical properties of composites. It has been reported that the dispersion of the reinforcements in the metal matrix can be significantly improved by molecular level mixing and in situ growth [32,33].

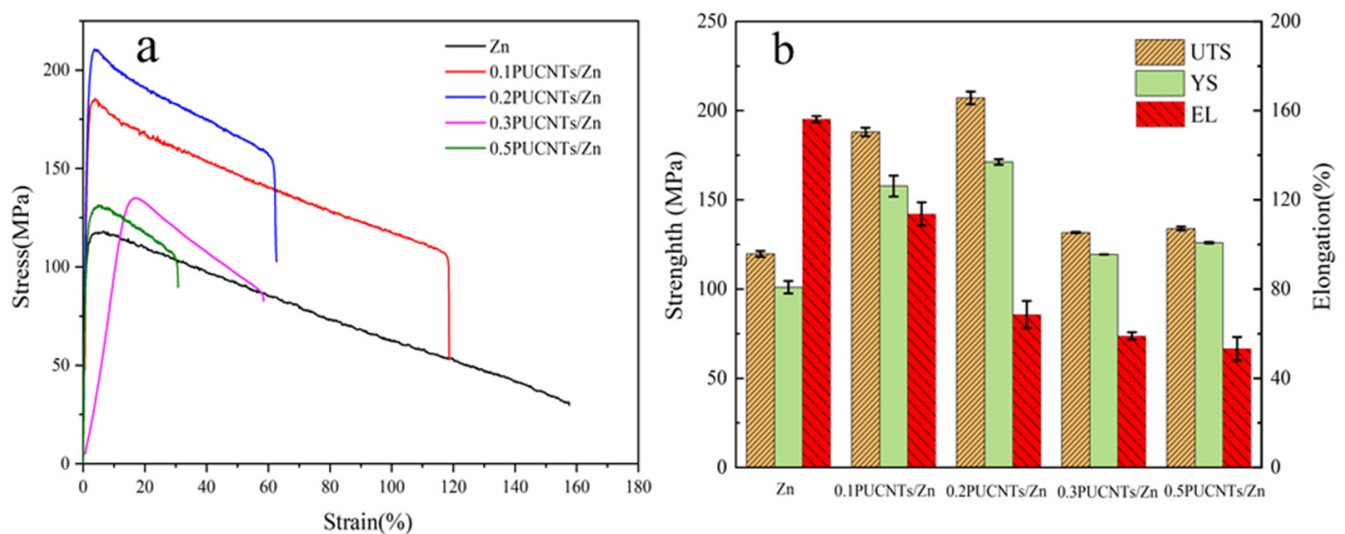


Figure 5. Mechanical properties of pure Zn and PUCNTs/Zn composites: (a) stress–strain curve; (b) tensile properties.

Figure 6 shows the fracture morphologies of pure Zn and PUCNTs/Zn composites after tensile fracture. From Figure 6a, it can be clearly seen that a few dimples appear on the fracture morphology of pure Zn; many fine grains are distributed on the fracture due to grain boundary slip (yellow circle in Figure 6a) [34,35]. The EBSD microstructure of pure Zn after rolling and tensile tests is shown in Figure 7. It can be seen from Figure 7a that the grain size of the rolled samples is not uniform, there are small broken grains shown in the A region, and the B region has fine recrystallized grains along the grain boundaries. The minimum grain size is 0.5 μm and the maximum grain size is 16.5 μm . Figure 7b shows that the grain refinement is obvious after tensile fracture, and the equiaxed grains are significantly increased compared with those before tensile fracture. Figure 7e,f are the corresponding kernel average misorientation maps, from which the deformation band inside the grains can be clearly seen. After the tensile test, the misorientation of pure Zn decreases. The above results indicate that the dynamic recrystallization of pure zinc occurs during room temperature stretching, which helps to relieve the accumulated stress, thus making the alloy have good plasticity. This is consistent with the conclusion of Shi [36]. It can be seen from the pole figure (PF) calculated from the corresponding EBSD map that the as-rolled sample has a strong basal texture with a maximum texture strength of 19.51 (Figure 7c). During the stretching process, the texture is significantly weakened due to the occurrence of dynamic recrystallization. The $\{0001\}$ pole is distributed near the ND, and the texture expands. Compared with the rolled sample, the texture strength decreases significantly. The maximum texture strength is 8.69 (Figure 7d).

The fracture morphologies of the PUCNTs/Zn composites are shown in Figure 6b–d, and it can be observed that PUCNTs exhibit different morphologies in the Zn matrix. Figure 6b,c shows that the fracture or pull-out of PUCNTs was observed on the fracture surface, indicating that load transfer is one of the strengthening mechanisms. When the content of PUCNTs is 0.5 wt%, the agglomeration of PUCNTs is observed on the fracture surface of the composite (Figure 6d), which will weaken the bond between Zn and the PUCNTs. When the composite is subjected to load, it is easy to cause cracks to occur at the weak interface, thereby reducing the load transfer efficiency. Therefore, adding appropriate reinforcements can effectively improve the mechanical properties of PUCNTs/Zn composites.

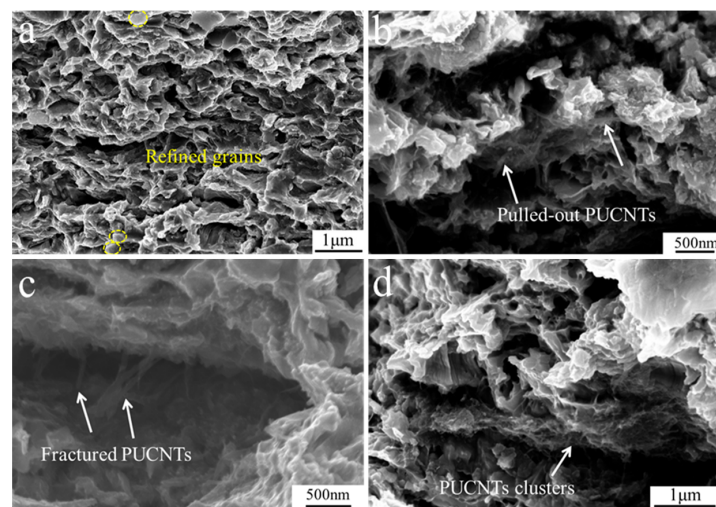


Figure 6. Fracture morphologies of pure Zn and PUCNTs/Zn composites: (a) fracture morphologies of pure Zn; (b) and (c) fracture morphologies of 0.2 PUCNTs/Zn composites; (d) fracture morphologies of 0.5 PUCNTs/Zn composites.

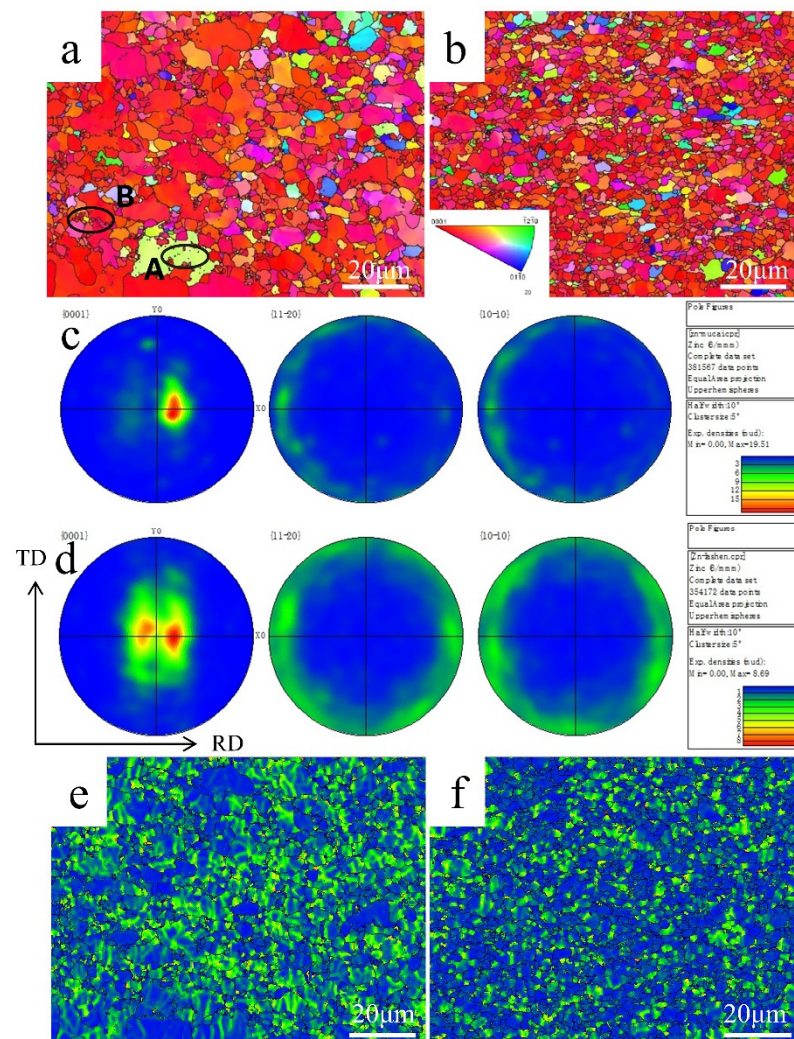


Figure 7. EBSD microstructure of pure Zn: inverse pole figure (a,b); pole figure (c,d); and kernel average misorientation maps (e,f). Rolled (a,c,e); stretched (b,d,f).

3.4. Enhancement Mechanism

Understanding the strengthening mechanism of CNTs/MMCs will help to further clarify the strengthening effect of PUCNTs/Zn composites. Several possible strengthening mechanisms have been proposed for CNTs/MMCs: (1) Load transfer strengthening; (2) Dislocation strengthening due to thermal mismatch; (3) Grain refinement; (4) Orowan strengthening. Since SPS is able to fully consolidate the composites at a shorter holding time, this largely prevents significant changes in grain size [37]. Therefore, the grain refinement effect is negligible. The strength of the composite material (σ_c) is expressed by the following equation:

$$\sigma_c = \sigma_m + \Delta\sigma_{Orowan} + \Delta\sigma_T + \Delta\sigma_{L.T} \quad (1)$$

where σ_m is the tensile strength of the matrix (~118 MPa in this study), and σ_{Orowan} , σ_T and $\sigma_{L.T}$ are the contributions of Orowan strengthening, thermal mismatch strengthening and load transfer strengthening, respectively. In order to further understand the difference of different strengthening factors in PUCNTs/Zn composites, it is necessary to calculate the contribution of each strengthening mechanism to the strengthening effect.

Due to the large aspect ratio of PUCNTs, we believe that load transfer plays a crucial role in the strengthening mechanism of PUCNTs-reinforced metal matrix composites. The strengthening effect of load transfer can be calculated using the following equations [38,39]:

$$\Delta\sigma_{LT} = \sigma_f V_f \left(\frac{l}{2l_c} \right) - \sigma_m V_f \quad (l < l_c) \quad (2)$$

$$\Delta\sigma_{LT} = \sigma_f V_f \left(1 - \frac{l_c}{2l} \right) + \sigma_m V_f \quad (l \geq l_c) \quad (3)$$

$$l_c = \sigma_f \left(\frac{d}{\sigma_m} \right) \quad (4)$$

where d , σ_f , V_f , and l are the diameter (~46.1 nm according to Figure 1b), tensile strength (30 GPa) [38], volume fraction (0.8 vol%) and length (~5.3 μm) of PUCNTs, respectively; the calculated critical length l_c is 11.7 μm . Since l is smaller than l_c , Equation (3) can be used to calculate the load transfer enhancement effect of PUCNTs/Zn composites.

Thermal mismatch strengthening is the strengthening of high-density dislocations at the interface due to the mismatch of thermal expansion coefficients between the reinforcing material and the matrix. In PUCNT reinforced Zn matrix composites, the thermal expansion coefficient of the Zn matrix is larger than that of PUCNTs ($19.3 \times 10^{-6}/\text{K}$ for Zn and $2.7 \times 10^{-6}/\text{K}$ for PUCNTs) [38], and during the plastic deformation process A large number of dislocations will be generated, hindering the migration of grain boundaries, thus playing a positive role in the strengthening of composite materials. According to the revised model, the strengthening effect of thermal mismatch strengthening on PUCNTs/Zn composites can be estimated [40]:

$$\Delta\sigma_T = 1.25Gb \sqrt{\frac{12\Delta CTE\Delta T V_f}{bd_p}} \quad (5)$$

$$d_p = \sqrt[3]{\frac{3ld^2}{2}} \quad (6)$$

where G is the shear modulus of the matrix (31.4 GPa for Zn), b is the Burger vector of the matrix (2.7×10^{-4} μm for Zn), ΔCTE is the difference in thermal expansion coefficient between the reinforcement and the matrix, ΔT is the difference between processing temperature and room temperature, and d_p is the effective reinforcement particle diameter.

PUCNTs inhibit the propagation of dislocations, thereby enhancing the strength of the composites, which can be expressed through the Orowan mechanism. The Orowan reinforcement effect can be calculated according to the Orowan–Ashby equation [14]:

$$\Delta\sigma_{\text{Orowan}} = \frac{0.13Gb}{\lambda} \ln\left(\frac{d_p}{2b}\right) \quad (7)$$

$$\lambda = d_p \left(\sqrt{\frac{\pi}{2V_f}} - 1 \right) \quad (8)$$

where λ is the effective planar inter-particle spacing. Substituting the corresponding parameters into the above equations to calculate the $\Delta\sigma_{L,T}$, $\Delta\sigma_T$ and $\Delta\sigma_{\text{Orowan}}$ of the PUCNTs/Zn composites are 53.4, 31.8 and 2.0 MPa, respectively. As shown in Figure 8, the estimated tensile strength values for the three strengthening mechanisms are close to the measured values. The results show that load transfer and dislocation strengthening caused by thermal mismatch are the main mechanisms for the strength improvement of PUCNTs/Zn composites.

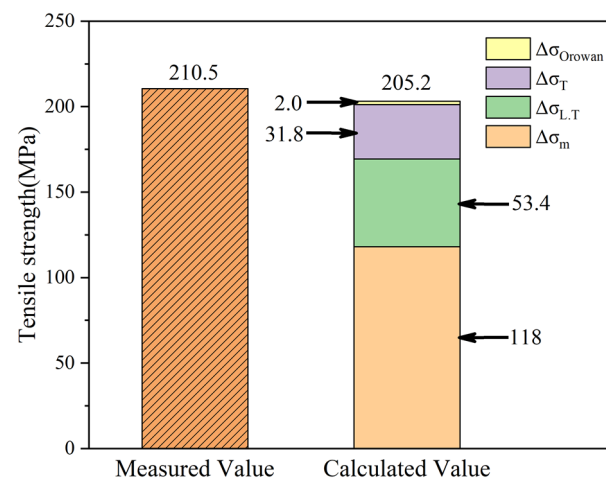


Figure 8. Calculated and measured values of tensile strength of PUCNTs/Zn composites.

4. Conclusions

The xPUCNTs/Zn ($x = 0, 0.1, 0.2, 0.3$ and 0.5 wt%) composites were successfully prepared by chemical unzipping and spark plasma sintering in this research. Compared with pure Zn, the mechanical properties of PUCNTs/Zn composites are significantly improved. The maximum tensile strength and yield strength of PUCNTs/Zn composites were 210.5 and 169.7 MPa when the content of PUCNTs reached 0.2 wt%, which is 78.4% and 64.4% higher than those of pure Zn (118 and 103.2 MPa), respectively, while the elongation (62.6%) remained at a higher level. The strengthening mechanisms of PUCNTs/Zn composites are load transfer strengthening, thermal mismatch strengthening and Orowan strengthening, in which load transfer strengthening plays a dominant role.

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