Microstructure and Mechanical Properties of MWCNT/Ti6Al4V Composites Consolidated by Vacuum Sintering

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Abstract:

Ti6Al4V alloys with low weight, high corrosion resistance, high melting point, high biocompatibility and unique mechanical properties have been receiving great attention for wide applicability in many industry fields such as automobiles, aerospace and biomedical. However, Ti6Al4V tends to be easily oxidized at high temperature, exhibit low thermal conductivity, low hardness and low yield strength and thus have led to the limitation of applicability in many industries. In this study, we have fabricated Ti6Al4V matrix composites reinforced with multi-walled carbon nanotubes (MWCNT) to enhance the hardness and yield strength. Vacuum sintering technique has been used to prepare MWCNT/Ti6Al4V composites. Microstructural and phase studies indicated that the composite structure consists of two main phases including α-Ti and β-Ti and MWCNTs were uniformly dispersed in Ti6Al4V matrix. The relative density of composite decreases as the CNT content increases as resulted from the porous structure of the CNT, which limits the aggregation process of the composite. When the CNT content increased, the hardness and yield strength of the composite increased, reaching maximum values of 378 HV and 356 MPa with 2 vol.% MWCNTs, which are nearly 16 and 38% higher than those of Ti6Al4V alloy. The enhancement in hardness and compressive strength is attributed to the good mechanical properties of MWCNTs and load transfer effect from Ti6Al4V alloy matrix to reinforcement material.

Keywords: Ti6Al4V, MWCNT, Composite, Microstructure, Hardness.

1. Introduction

By combining the outstanding properties of both base metals and reinforcement materials, metal matrix composites (MMCs) usually exhibit the unique properties that cannot be obtained by single-phase materials. Therefore, MMCs are one of the important materials, which are increasingly widely used in aerospace, national security, machine manufacturing, electrical, electronics, etc. Since its discovery and publication in 1991, carbon nanotubes (CNTs) have shown many preeminent properties such as high mechanical properties, good thermal and electrical conductivity [1]. CNTs have been used as reinforcement materials in polymer, ceramic and metal to combine the good properties of CNTs and matrix materials [2-5]. Recently, the studies have been noticed and developed in using CNTs for MMCs. Numerous published studies have demonstrated that CNTs can improve the mechanical, thermal and electrical properties of metals and alloys such as aluminum [6-10], copper [11-
15], magnesium [16, 17] and nickel [18]. Among metals and alloys, titanium and titanium alloys have lightweight, good corrosion resistance, high melting point, biological compatibility and good mechanical properties even at freezing temperatures. Therefore, titanium (Ti) and titanium alloys have been receiving great attention due to their wide applicability in industries such as automotive, aerospace and biomedical [19]. However, previous research results have shown that titanium and its alloy usually have low thermal conductivity, hardness and low strength. These issues limited the applicability of titanium and its alloys in some industries and thus needing to combine them with some nanosized reinforcement materials to improve the properties [20-24].

In this study, we fabricated Ti6Al4V matrix composites reinforced with MWCNTs to enhance the hardness and compressive strength. Powder metallurgy method with vacuum sintering technique has been used to prepare the composites. The effect of MWCNT concentration on the microstructure and mechanical properties of the composites are investigated and presented.

2. Materials and Experimental Procedures

2.1. Materials

Multi-walled carbon nanotubes (MWCNTs) synthesized by chemical vapor phase deposition technique is used as reinforcement material [25]. Ti6Al4V commercial powder with an average particle size of about 45 µm provided by Kiswel, Korea is used as a matrix material.

2.2. Fabrication of MWCNT/Ti6Al4V composites

Firstly, MWCNTs were treated in a mixture of acid HNO3:H2SO4 (1:3) at a temperature of 70°C for 5 hours to attach –COOH functional group on the surface of MWCNTs. After functionalization, MWCNT-COOH was dispersed in ethanol with a ratio of 1 g/l by a tip sonication technique for 45 minutes. Ti6Al4V powder is then slowly introduced into MWCNT solution with different concentration and dispersed by tip sonication. The obtained solution containing MWCNTs and Ti6Al4V is rapidly cooled in liquid N2 medium. After that, the drying process in the vacuum environment was used to remove the steam contained in the mixture aiming to obtain the final product is MWCNT/Ti6Al4V powder. The concentration of MWCNTs included in the composite powder was calculated to be 1 vol.% and 2 vol.. The obtained powders were compacted as a compact size of φ22×10 mm which was carried out on a hydraulic press, with a pressure of 200 MPa hold for 20 seconds. Finally, the pressed sample was sintered in a vacuum (~ 2×10⁻³ Pa) at a temperature of 1100°C for 3 hours to obtain a MWCNT/Ti6Al4V composite. Ti6Al4V material samples without MWCNTs were also prepared with the same conditions to compare and evaluate results.

2.3. Characterizations

The microstructure, morphology, of the composites were investigated by scanning electron microscopy (SEM) (Hitachi S-4800) and high-resolution electron microscopy (HRTEM) (JEOL 2100F). The functional groups were analyzed by Fourier transform infrared spectroscopy - FTIR (Prestige 21-SHIMADZU) within a range of 1000 - 4000 cm⁻¹ wave. Raman spectra were measured by iHR550 Jobin-Yvon device under the excitation wavelength of Ar laser at 514 nm. The density was determined by the Archimedes method and the hardness of the material was measured on AKV-CO/Mitutoyo. The compressive strength tests
were measured on cylindrical specimens with 4 mm in diameter and 8 mm in height using a universal testing machine (Tinius Olsen Super L120).

3. Results and Discussion

Fig. 1a shows the morphology of MWCNTs observed by SEM and HRTEM techniques. The image shows that MWCNTs has an average diameter of about 15-20 nm, the wall is formed from 12-14 parallel atomic layers. Since MWCNTs is about a few ten nanometers in diameter and micrometers in length, MWCNTs can be considered a fibrous material. Thus, MWCNTs tend to clump in solution, forming clusters, making it difficult to separate strands and evenly disperse MWCNTs onto metal particles. In order to solve this problem, MWCNTs were functionalized to attach –COOH functional group to the surface, making it easier for separating them in polar media such as water or alcohol.

FTIR spectra of MWCNTs after surface functioning with –COOH functional group is shown in Fig. 1b. As observed, in addition to the characteristic peak for C= C link at 1555 cm⁻¹, a number of peaks that are characteristic of the bond C=O at 1730 cm⁻¹ and C-O at 1030 cm⁻¹. In particular, the C=O and C-O bonds are characteristic peaks for the –COOH functional group. Thus, it can be concluded that the COOH functional group has been attached to the surface of MWCNTs by treating it with the mixture of acids including H₂SO₄ and HNO₃.

Fig. 2a and 2b show the distribution of MWCNTs on the surface of Ti6Al4V particles after being dispersed by the combination of tip sonication and rapid cooling. As can be seen, MWCNTs were covered around Ti6Al4V particles, indicating that MWCNT is uniformly dispersed in the mixed powder. Fig 2c and 2d show the fracture surface morphology of composite after sintering containing 2 vol.%MWCNTs. Some MWCNTs in Ti6Al4V alloy matrix were also observed individually on the fracture surface. This demonstrated that the good interfacial bonding between MWCNTs and Ti6Al4V alloy was formed. In such a manner improvement of the load transfer from matrix to MWCNTs leads to the better mechanical properties of the composites.

Raman spectra of graphite structure are represented by a peak of the vibration mode at 1575 cm⁻¹. The Raman spectrum of CNT has a typical peak at 1575 cm⁻¹, called the G peak, which represents the graphite structure of MWCNTs.
Fig. 2. (a,b) MWCNT/Ti6Al4V composite powder and (c,d) Dispersion of MWCNTs inside Ti6Al4V matrix after sintering.

Fig. 3. (a) Raman spectra of MWCNTs, MWCNT-COOH, MWCNT/Ti6Al4V powder and MWCNT/Ti6Al4V composite; (b) XRD patterns of MWCNTs, Ti6Al4V, 1%MWCNT/Ti6Al4V and 2%MWCNT/Ti6Al4V composite.

The disorder or the occurrence of sp$^3$ hybridization defects leads to the vibration mode at 1350 cm$^{-1}$, this peak is called D peak or defect peak. The intensity ratio of peak D and peak G ($I_D/I_G$) is usually used to estimate the structure of CNTs. The higher the $I_D/I_G$ value means the greater the defect in the CNT structure. Fig. 3a shows Raman spectra of MWCNTs, MWCNT-COOH, MWCNT/Ti6Al4V powder and MWCNT/Ti6Al4V composite. The peak D at around 1350 cm$^{-1}$ was determined for all samples. Peak G of as-received MWCNTs and
CNT-COOH is detected at 1579 cm\(^{-1}\) and 1592 cm\(^{-1}\), respectively. The movement of the G peak toward the higher wavenumber is attributed to the functionalization process that caused more defects on the graphite structure. Besides, the \(I_D/I_G\) ratio of CNT-COOH of 1.06 is higher than that of as-received MWCNTs (0.92). This proves that the strong acidification function has caused more defects in the CNT structure. The \(I_D/I_G\) ratio of MWCNT/Ti6Al4V powder is calculated to be 1.05, which is slightly higher than that of MWCNT-COOH. This implied that the mixing process with the tip sonication caused a few defects to MWCNTs structure. Similarly, the increase in the \(I_D/I_G\) ratio to 1.12 of MWCNT/Ti6Al4V composite is attributed to the effect of the high temperature treatment during the sintering process.

The phase composition of the composites is determined by X-ray diffraction technique. Fig. 3b is XRD patterns of MWCNTs, Ti6Al4V and MWCNT/Ti6Al4V composites. As can be seen from the patterns, only typical peaks of graphite are detected for MWCNTs. The XRD patterns of the Ti6Al4V and MWCNT/Ti6Al4V composites are relatively similar, including some characteristic peaks of \(\alpha\)-Ti at 2\(\theta\) = 35.15\(^o\), 38.72\(^o\) and 40.26\(^o\) corresponding to (100), (002) and (101) plane, respectively. The typical peak of \(\beta\)-Ti at 39.45\(^o\) corresponding to the (002) plane was also found. The obtained results indicated that Ti6Al4V and MWCNT/Ti6Al4V composite have \(\alpha + \beta\) structure. No presence of the typical peaks for MWCNTs in composite samples was detected, this can be explained by the fact that the MWCNT concentration in the composite is quite low (2 vol.\%) that is lower than the resolution of the measurement device.

![Fig. 4.](image)

**Fig. 4.** (a) Density and (b) hardness of MWCNT/Ti6Al4V composites containing different MWCNT concentration.

Fig. 4a shows the dependence of the density and relative density of composites on the MWCNT concentration. The relative density of the samples is determined by taking the average of five measured values. When MWCNT is added, the density of composites decreases. The relative density of Ti6Al4V vacuum sintered alloy is ~ 93%. The relative density then decreases to 91.5 and 89.3% corresponding to the composite containing 1 vol.% and 2 vol.% MWCNT concentration, respectively. This means that the relative density of the composites is decreasing when MWCNT concentration increase. This result probably comes due to the porous structure of MWCNTs that limits the consolidation process of the composites. Fig. 4b shows the hardness of MWCNT/Ti6Al4V composites with different CNT concentrations. Realizing that when the CNT concentration increases, the hardness of the composites increases and reaches the maximum value of 378 HV for the composite containing 2% MWCNT, which is nearly 18% higher than that of Ti6Al4V alloy hardness (325 HV). The increase in the hardness of the composites with the addition of MWCNTs
could result from the nanometer-sized MWCNTs acted as the keys hindered the movements of dislocations [26]. Furthermore, mismatch strains properly develops at the MWCNT/matrix interfaces due to the difference of the coefficients of thermal expansion between MWCNTs and the Ti6Al4V matrix will block the movement of the dislocations to enhance the hardness of the composites [27].

Fig. 5a shows the typical compressive stress-strain curves of composites with different MWCNTs concentration. As can be seen, the compressive strength of the composites increases with an increase in MWCNT concentration. Fig. 5b shows the enhancement of the yield strength of the composites. The yield strength of the composites increases by up to 24 and 38% corresponding to the composites containing 1 vol.% and 2 vol.% MWCNT, respectively. The obtained results indicate that addition and uniform dispersing of CNTs over a Ti6Al4V alloy matrix can be the key factors which are leading to an enhancement of the composite’s hardness and compressive strength. Besides, the difference in coefficients of thermal expansion of the Ti6Al4V alloy and MWCNTs could cause some thermal expansion mismatches in the composites during the sintering process. The formation of the dislocations at the MWCNT/Ti6Al4V interface caused by the mismatch strains leads to work hardening of the matrix [28]. Munir and coworkers have also investigated the enhancement in compressive yield strength of MWCNT/Ti composites and found that the addition of MWCNTs significantly improved the dislocations at the interfaces between MWCNTs and Ti matrix by the thermal expansion mismatches [29]. However, it is difficult to observe the formation of the dislocation caused by mismatches. Further works will be done on the precise detection of the development of dislocations caused by the mismatch strains at the CNT/Ti6Al4V interfaces using transmission electron microscopy (TEM) to clarify the matter. Besides, the enhancement in the mechanical properties of the composites with the addition of MWCNTs results from some other strengthening mechanisms such as load transfer, grain refinement, Orowan looping as discussed in several earlier reports [30-32].

![Fig 5. (a) Compressive stress-strain curves and (b) yield strength of MWCNT/Ti6Al4V composite containing different MWCNT concentration.](image)

4. Conclusion

We have fabricated the MWCNT/Ti6Al4V composites by powder metallurgy method with vacuum sintering technique. The composite structure consists of two main phases: α-Ti and β-Ti. The density of composites decreases when the CNT content increases due to the porous structure of CNT material that limited the consolidation process. The obtained results
reveal that MWCNTs were uniformly dispersed inside the Ti6Al4V alloy matrix. Composites containing MWCNTs showed an improvement in hardness and yield strength up to 18 and 38% respectively, compared to those of Ti6Al4V alloy. The enhancement is attributed to the uniform dispersion and strengthening due to the effect of MWCNTs addition. However, the composite prepared by vacuum sintering has a relatively low density (~ 90%). Therefore, in order to improve the reinforcement ability of MWCNTs for Ti6Al4V alloy matrix, it is necessary to apply the advanced sintering techniques such as isostatic hot pressing or spark plasma sintering.

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5. References

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Сажетак: Легуре Ti6Al4V које су мале тежине, високе отпорности на корозију, високе температуре топљења, високе температуре проводљивост, малу тврдоћу и због тога имају важну улогу због распрострањене примење у разним гранама индустрије, као што су аутомобилска, ваздухопловна и биомедицинска. Међутим, Ti6Al4V имају тенденцију да лако оксидују на високим температурама, имају ниску температурску проводљивост, малу тврдоћу и због тога имају ограничења у примени. У овом раду смо синтетисали матрикс Ti6Al4V композита који је побољшан карбонским нано-тубама (MWCNT) да би се побољшала тврдоћа и напон течења. Техника синтеровања у вакууму је коришћена за припрему композита MWCNT/Ti6Al4V. Микроструктурна анализа и испитивање фазног састава указују на то да се структура композита састоји из две фазе, а-Ти и β-Ти а MWCNTs су уједначено дисперговане у матриксу Ti6Al4V. Релативна густина композита опада са порастом садржаја нано-туба што потиче од порозних нано-туба, што лимитира процес агрегације композита. Када расте удео нано-туба, тврдоћа и напон течења композита расту, достигнући максималне вредности 378 HV и 356 MPa са 2 vol.% MWCNTs, што је скоро 16 и 38% више од саме легуре Ti6Al4V. Побољшање у тврдоћи и напону течења је приписано добром механичким својствима MWCNTs.

Кључне речи: Ti6Al4V, MWCNT, композити, микроструктура, тврдоћа.

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