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Structural integrity and dispersion characteristics of carbon nanotubes in titanium-based alloy

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Abstract. Over the years, carbon nanotubes have attracted much attention in engineering materials research due to their outstanding and superlative properties. Owing to the demands for lightweight materials with excellent mechanical and thermal properties for diverse industrial applications encouraged the incorporation of carbon nanotubes into titanium alloys. However, there are various challenges associated with the incorporation of carbon nanotubes into titanium alloys which includes; uniform dispersion and retaining the structural integrity of carbon nanotubes after dispersion. Past works have emphasized the importance of homogeneous dispersion with less structural damage to the carbon nanotubes in the various metal matrix. Therefore, this research focused on dispersion of 0.5 wt. % multiwalled carbon nanotubes in Ti6Al4V using low energy ball milling and evaluating the dispersion characteristics and structural integrity of MWCNTs in Ti6Al4V after dispersion. Various characterization techniques such as high-resolution transmission electron microscopy, scanning electron microscopy, X-Ray diffraction and Raman spectroscopy were adopted to ascertain the microstructural evolution, morphology, interfacial reaction and structural integrity of the carbon nanotubes in the Ti6Al4V powders before and after dispersion. The results indicated homogeneous dispersion of carbon nanotubes with less structural damages which are confirmed from the (ID/IG) ratio of the Raman spectra and the TEM images.

1. Introduction

The quest for materials with extraordinary properties for advanced engineering applications have unveiled the benefits of incorporating carbon nanotubes (CNTs) into metal matrix. Since the discovery of carbon nanotubes by Iijima [1] in 1991, they have accomplished unreasonable feats in materials research communities and this is due to their unique and superlative mechanical and thermal properties [2,3]. However, CNTs are recognized for their light weight (~1.7–2.0 g/cm^3), tubular morphology and ultra-high aspect ratios (~100–100,000). These have captured the interest of researchers to exploit their superlative mechanical properties (such as Young's modulus in the tera Pascal (TPa) range), strength up to 100 GPa to synthesize advanced light weight, high strength alloys and composites for aerospace and automotive industries [4]. In addition, the distinguishing properties of CNTs are generally ascribed to their seamless cylindrical morphology, quasi-one-dimensional (1D) structure, graphite-like arrangement of the carbon atoms in the shells and existence of strong sp^2 carbon–carbon (C–C) bonds in their outer shells [3,5].

Owing to the demands for engineering materials with improved properties, titanium and its alloys have attracted considerable attention for diverse applications in aerospace, petrochemical and many other industries [6]. This is due to their unique properties; relatively low densities, high-specific strength, biocompatibility, nonmagnetic properties, high melting point, corrosion resistance and adequate creep resistance at temperatures up to 400 ^{0}C [7]. However, it has been reported from past research that they possess some inferior properties such as poor hardness, stiffness when compared with steels and super nickel alloys, ease of oxidation and loss of mechanical properties at elevated temperature [7] which have encouraged the incorporation of CNTs into their structure for properties enhancements.

During the fabrication of CNTs reinforced titanium matrix composites (TMCs), homogeneous dispersion of the CNTs into the titanium-based matrix without compromising its structural integrity is a paramount challenge. Carbon nanotubes have the tendency to agglomerate into clusters within the titanium-based matrix which is due to their nanoscale dimensions and the strong Van der Waals forces among individual tubes [8]. However, it is essential to uniformly disperse CNTs in titanium-based matrix to access their unique load and heat bearing efficiency in synthesized CNT-TMCs.

In recent times, efforts have been made to homogeneously disperse carbon nanotubes in various metal matrix by adopting different dispersion techniques; solution ball milling [3], ultrasonication [9] functionalization of the CNTs [10], high energy ball milling (HEBM) [5], and gentle milling [11]. The HEBM has proved to be most efficient, effective and economical technique to uniformly disperse CNTs in the metal matrix [12]. However, other research have reported the reactive effects of harsh milling conditions of HEBM on the structural integrity of CNTs [13]. This milling technique leads to the formation of non-sp^2 phase in the C-C bonds of the CNTs resulting in the compromise of the superlative properties, weakening of the strong sp^2 bond, the formation of vacancies and open edges in the CNTs [14]. In addition, the non-sp^2 phase are potential sites for the formation of interfacial reactions at the metal-CNTs interface that promote the creation of titanium carbide phases [3]. Meanwhile, a good metal-CNTs interface is highly desirable to enhance the strengthening mechanism and properties of the resulting composites [15]. In a bid to uniformly disperse multiwalled carbon nanotubes (MWCNTs) in titanium-based matrix without compromising its structural integrity after dispersion, gentle milling approach was adopted in this work.

2. Materials and Method.

2.1 Starting materials

The starting powders utilized for this study were argon atomized, prealloyed Ti6Al4V (~25 μm particle size), supplied by TLS Technik GmbH & Co., Germany and MWCNTs supplied by Nanocycl Belgium with average diameter of 9.5 nm and length of 1.5 μm.

2.2. Powders preparation by gentle milling (GM)

A gentle mill (Retch PM 100, Germany) was utilized to disperse 0.5 wt.% MWCNTs into the Ti6Al4V matrix. This was done by charging the starting powders in a stainless-steel vial (250 ml, inner diameter (ID) = 100 mm) with stainless steel balls of two dissimilar sizes (diameter (d) = 10 and 5 mm). The various sizes of the steel balls were adopted to prevent cold welding of powder particles and enhance the collision energy introduced into the powders. The ball to powder ratio (BPR) was maintained at 5:1. In addition, the milling was carried out for 4 hours at a speed of 150 rpm with a relaxation time of 10 minutes to prevent the samples from heating up. The admixed powders were collected and characterized after milling.

2.3 Characterization of as-received and admixed powders

The morphology of the starting and admixed powders was characterized using scanning electron microscopy (Carl Zeiss Sigma FESEM) equipped with energy dispersive X-ray spectrometry (EDX). Similarly, transmission electron microscopy (JEOL-Jem 2100) was used to characterize the

morphology and structural integrity of the MWCNTs before and after dispersion. The phase identification and structural changes of the powder mixtures were characterized by X-ray diffractometer (XRD, Rigaku D/max-rB) and Raman spectroscope (In-Via Raman microscope, Renishaw Plc) respectively. The XRD profiles of as-received powders and admixed powders were scanned using Cu-Kα(λ= 0.154 nm) radiation at a scanning rate of 1°/min over the angular range of 20–90°. Raman scattering was obtained in the spectral range of 200–1800 cm^{-1} on multiple powder mixtures and admixed powder at least 10 various positions with an acquisition of 50 s using a 514 nm laser (laser power = 5.63 mW). The intensity of Raman peaks and their conforming positions were acquired by deconvoluting the Raman spectra into two Gaussian peaks using WITec 2.0 software.

3. Experimentation Results and Discussion

3.1 Dispersion of MWCNTs in Ti6Al4V

The morphology of the as-received Ti6Al4V and MWCNTs powders as shown in Figure 1 (a -d). Due to the strong van der Waal forces between individual MWCNTs, they tend to agglomerate into clusters. Therefore, adequate energy is required to disperse MWCNTs into the Ti6Al4V matrix, and to de-entangle them by reducing the effects of the strong van der Waal forces.

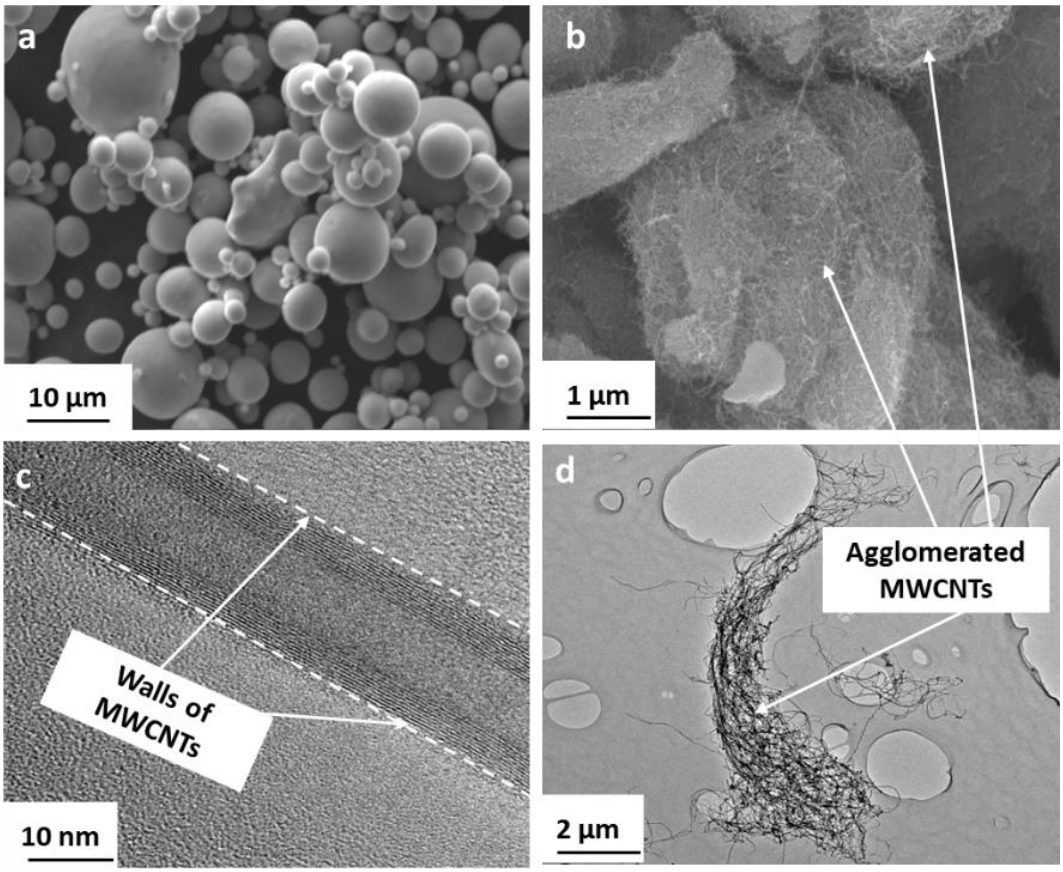

Figure 1. HRSEM (a &b) and HRTEM (c &d) images of the Powders Ti6Al4V (a) and MWCNTs (c-d).

Similarly, the SEM images of the admixed powder containing 0.5 wt. % MWCNTs in Ti6Al4V after milling for 4 h at a speed of 150 rpm is shown in Figure 1 a and b. It was observed that the MWCNTs were dispersed in the Ti6Al4V. However, some level of agglomerations was observed and this was

ascribed to the strong Van der Waal forces between the individual MWCNTs, high surface area and aspect ratios which inhibit the full homogeneous dispersion of MWCNTs in the TiAl4V [3].

Additionally, it was observed from the SEM (a & b) and TEM (c & d) images of the admixed powders in Figure 2 (a-d) that the MWCNTs were relatively dispersed and embedded in the Ti6Al4V particles, these characteristics was ascribed to the adopted milling parameters that exerted optimum energy to disperse and embed the MWCNTs in the Ti6AL4V particles. However, some level of bundling of MWCNTs were observed when the magnification of the samples was increased from 500 X in figure (2a) to 20000 X in figure (2b). Despites the clustering of the MWCNTs on some portion of the Ti6Al4V particles, the level of recorded dispersion may help to improve the load bearing capability and some other desired properties of the Ti6Al4V matrix when sintered. Moreover, slight deformation to the wall of the MWCNTs (2d) were observed and this is ascribed to the continuous shearing force exerted by the milling balls on the walls of the nanotubes during milling operation.

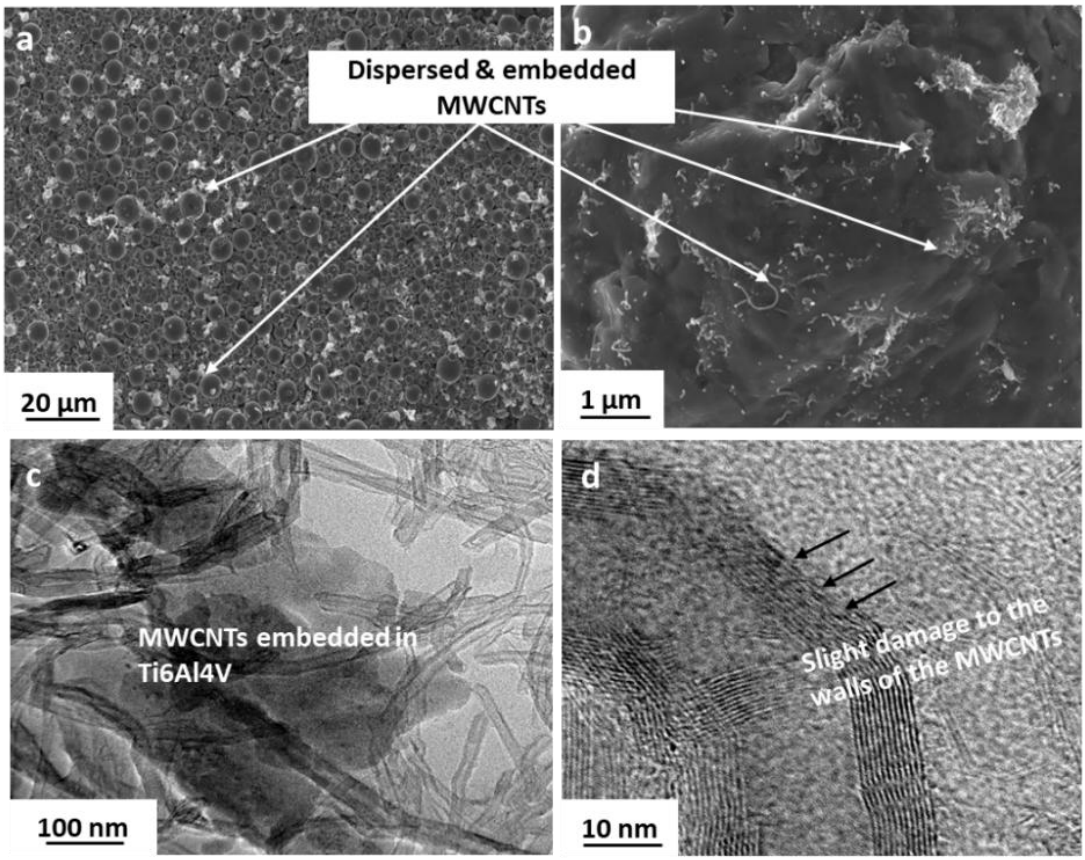

Figure 2. HRSEM (a & b) and HRTEM (c & d) images of the Admixed 0.5 wt. % MWCNTs in Ti6Al4V

3.2 Phase analysis of the MWCNTs in Ti6Al4V

X-ray diffraction (XRD) techniques was utilized to identify the various phases, structural changes and the evolution of the crystalline phases in the as-received and admixed MWCNT-Ti6Al4V. Figure 3 shows the XRD patterns of the starting powders and ball milled powder mixtures. The XRD patterns for the admixed powders depicted only slightly increased peaks of the α-Ti. Since the volume fraction of the MWCNTs in the admixed powders was significantly low (0.5 wt.%). Additionally, the XRD analysis did not identify any MWCNTs peaks in the admixed powders and this may be ascribed to the substantial difference in the mass absorption coefficient for Cu Kα radiations of Ti and carbon (C) which are 208 and 4.6 m^2/g, respectively [16]. However, XRD peaks of the admixed powder did not

depict any formation of carbide phase which may likely be formed during harsh milling condition. The formation of carbide phase is usually traceable to the destruction or damage of the MWCNTs structure where vacancies are formed which act as potential sites for the formation of carbide phases (TiC).

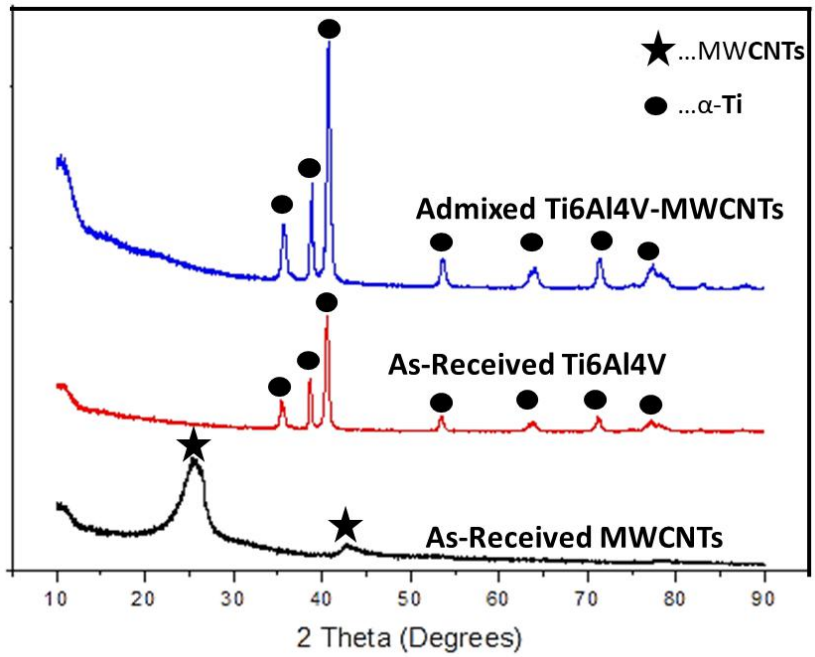

Figure 3. XRD Result of As-received MWCNTs, Ti6Al4V and admixed powders

3.3 Raman analysis of MWCNTs in Ti6Al4V

The structural integrity of the dispersed MWCNTs in Ti6Al4V was determine by Raman spectroscopic technique. This technique is used to characterize the sp^2 carbon structure of the MWCNTs in the admixed powder. The effect of processing method on the MWCNTs during dispersion is reflected on the Raman spectra.

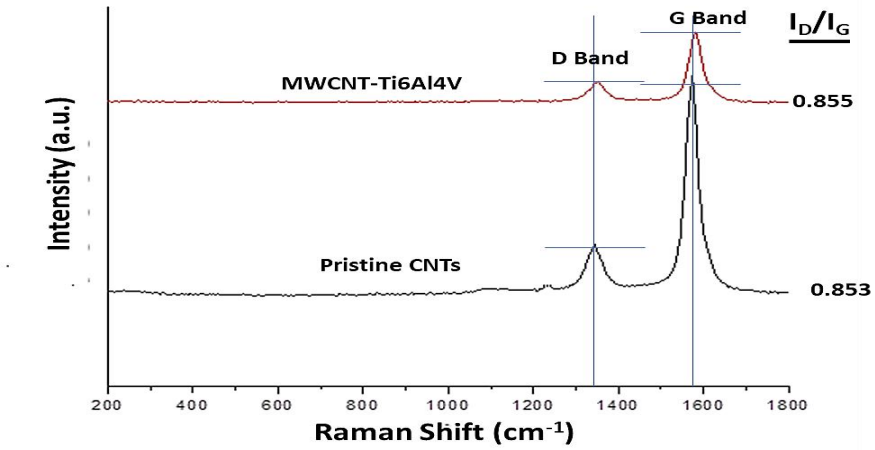

Figure 4. Raman Spectra of the Pristine MWCNTs and Admixed Powders

The Raman spectrum of the pristine MWCNTs is shown for comparison of the effects of the adopted processing parameters on the structural integrity of the MWCNTs during dispersion in Ti6Al4V. As shown in Figure 4, the two graphitic peaks of interest were observed at 1344.9 and 1575.9 cm^{-1} in the Raman spectra of the pristine MWCNTs, which represents the D band and G band, respectively. The D band depicts the defect peak and it is related to the disorder in the C-C bond which is sometimes regarded as the non-sp^2 structural defects in the MWCNTs [3]. However, G-Band represent the in-plane stretching mode of C-C bonds and it indicates the degree of crystallinity in the MWCNTs [17]. From the Raman spectra of the pristine MWCNTs and admixed powders, it was observed that the I_D/I_G ratio is 0.853 and 0.855 respectively. This is an indication that there was a slight increase in the Raman peak ratio (I_D/I_G) to 0.855 which correspond to 0.2 percent increase and a slight movement of the G band to a higher wave number of 1581.8 cm^{-1}. The increased in the Raman peak ratio is an indication of a minimal deformation in the crystalline structure of MWCNTs during dispersion which is in conformity with the TEM result where slight damaged was observed at the walls of the MWCNTs in the admixed powder. However, the level of structural damages doesn't result in the formation of titanium carbide during dispersion which would have reflected as peaks between 200 and 800 cm^{-1} on the Raman spectra of the admixed powders [3]. In addition, non-sp^2 structural defects were not formed during dispersion and this is in conformity with the XRD results where no titanium carbide phase was recorded.

4. Conclusion

The adoption of gentle milling in incorporating MWCNTs into Ti6Al4V is a viable approach for composites production since it results in relative uniform dispersion of MWCNTs with minimal structural damages to the MWCNTs. This was achieved by milling at lower energy and controlling the heating up of the samples during milling. The TEM, Raman and XRD characterization results indicated that there were less structural damages to the MWCNTs and no unwanted phase was formed during milling operation. Additionally, the SEM results revealed homogeneous dispersion with less clustering of the MWCNTs.

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