# Characteristics of powder metallurgy pure titanium matrix composite reinforced with multi-wall carbon nanotubes

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## Abstract

By using pure titanium powder coated with un-bundled multi-wall carbon nanotubes (MWCNTs) via wet process, powder metallurgy (P/M) titanium matrix composite (TMC) reinforced with the CNTs was prepared by spark plasma sintering (SPS) and subsequently hot extrusion process. The microstructure and mechanical properties of P/M pure titanium and reinforced with CNTs were evaluated. The distribution of CNTs and in-situ formed titanium carbide (TiC) compounds during sintering was investigated by optical and scanning electron microscopy (SEM) equipped with EDS analyzer. The mechanical properties of TMC were significantly improved by the additive of CNTs. For example, when employing the pure titanium composite powder coated with CNTs of 0.35 mass%, the increase of tensile strength and yield stress of the extruded TMC was 157 MPa and 169 MPa, respectively, compared to those of extruded titanium materials with no CNT additive.

Fractured surfaces of tensile specimens were analyzed by SEM, and the uniform distribution of CNTs and TiC particles, being effective for the dispersion strengthening, at the surface of the TMC were obviously observed.

**Key words**: Ti powder, Carbon nanotubes, Spark plasma sintering, Extrusion, TiC

## Introduction

Carbon nanotubes (CNTs), found in 1970's by S. Iijima [1], have a potential to be used as attractive reinforcements of the composite materials because have a low density of 1.3 g/cm$^3$ and 973 GPa Young's modulus [1-3]. It is also well known that CNT also has excellent electrical and thermal conductivities [4]. Previous studies indicated characteristics of the metal matrix composites (MMCs) reinforced with CNTs, where industrial metals such as aluminum, magnesium, nickel, copper and their alloys were used [5-14]. Titanium (Ti) and titanium alloy are also interested as the matrix material because they are widely used in various industrial applications, for example, automotive, motorcycles, and airplane industries due to their high specific strength and Young's modulus. Their chemical and petrochemical applications are also excellent because of their high corrosion resistance [15]. On the other hand, when adding CNTs into metals as reinforcements, powder metallurgy (P/M) process is more suitable than ingot metallurgy (I/M) because the separation of CNTs from the molten metals easily occurs due to their buoyancy caused by the low density. Furthermore, the agglomeration of the bundled CNTs always exists in P/M composite materials because of their van der Waals force, which is attractive or repulsive between carbon atoms [16, 17]. One of the researchers in the previous study showed an effective preparation of un-bundled CNTs by using the zwitterionic surfactant solutions via wet process [18]. In this study, the microstructures and mechanical properties of P/M titanium matrix composite (TMC) reinforced with un-bundled CNTs by using the above wet process. It is strongly expected that the combination of Ti and CNTs will serve superior tensile strength to the conventional TMC. The strengthening mechanism of the composites with CNTs is discussed by their microstructures analysis and identification of the dispersoids.

## Experimental

Atomized pure Ti powders, having a mean particle size of 30 μm, was used as starting materials. The impurity contents of raw powder were Fe; 0.03, Si; 0.01, Mg; <0.001, Cl; <0.002, O; 0.21, N; 0.02, C; <0.01 mass%. Oxygen and carbon content of raw powders and extruded materials were measured by Inert gas fusion instruments- nitrogen-oxygen determination (LECO Co., TC-300), and carbon-sulfur determination (LECO Co., CS-200), respectively. The content of the other elements was by Inductively Coupled Plasma (ICP) analysis. The zwitterionic surfactant solution with CNT concentration of 3.0 mass% was prepared. Multi-wall CNTs with about 20 nm diameter and 5~10 $\mu$m length were employed in this experiment. Polar zwitterions generally had a high solubility in water, but a poor solubility in most organic solvents. 3-(N, N-dimethylstearylammonio) propanesulfonate, a typical linear zwitterionic surfactant, was used in this study. It had both hydrophobic and hydrophilic groups. Electrostatic interactions, having larger attractive forces than the van der Waals forces between CNTs, occurred at the hydrophilic because of the positive charge and negative charges on their headgroups. Therefore, the un-bundled CNTs existed in the zwitterionic surfactant solution [18]. Two kinds of the solutions containing 1 and 2 mass% CNTs were prepared by diluting the above solution with the CNT concentration of 3 mass% with the zwitterionic surfactant solution. Ti powders were dipped into each solution, and subsequently dried in oven at 373 K for 10.8 ks. The composite Ti powders coated with CNTs were obtained, and the individually independent CNT were observed on the powder surface as shown in Fig.1. Surfactant solids also existed, and should be removed before hot consolidation because they changed to gases at elevated temperature over 773K [19], and would cause the pores as material defects. From a viewpoint of the thermal resolution of the surfactant solids, the Ti composite powders with CNTs were consolidated in the carbon die (diameter; 43mm) by spark plasma sintering (SPS, Syntech Co. SPS-1030S) process with two-steps heating; 873 K for 3.6 ks for their removal and 1073 K for 1.8 ks for the vacuum sintering. The applied load during the heating was 20 kN and 41.6 kN, respectively. The sintered Ti composite compact, having a diameter of 43mm and thickness of 15mm, was heated at 1273 K for 180 s in argon atmosphere, and immediately served to hot extrusion. The extrusion ratio, speed and die temperature were 37, 3.0 mm/s and 673 K, respectively. The extruded titanium powder material bars with a diameter of 7 mm and length of 800 mm were prepared. The pre-heating at 1273K was enough for in-situ synthesis of titanium carbides (TiCs) by the reaction of Ti matrix and CNTs. Microstructure and phase characterizations were investigated by X-ray diffraction (XRD, Shimadzu XRD-6100), optical microscope and scanning electron microscope with energy dispersive spectrometry (SEM-EDS, JOEL, JSM-6500F). P/M extruded TMC materials were machined to tensile specimen bars with 3mm diameter and 15 mm gauge length, and three specimens for each material were evaluated at room temperature. The fractured surface of the specimens was observed by FE-SEM to investigate the dispersion strengthening mechanism by CNTs and in-situ TiCs.

## Results and Discussion

Chemical analysis on P/M extruded Ti material and composites reinforced with un-bundled CNTs indicates that the carbon content is <0.01 wt%, 0.183 wt%, 0.242 wt% and 0.351 wt%, respectively. This means that the content of dispersed CNTs of the TMC material is about 0.18 wt%, 0.24 wt%, and 0.35 wt% when using the zwitterionic surfactant solution with CNT concentration of 1, 2 and 3 mass%. This means that the content of MWCNTs coating Ti powder surface increases with increase in the CNT concentration of the solution. It is, however, impossible to lineally control their content by changing the solution concentration including CNTs. On the other hand, the oxygen content of materials is 0.26 wt%, 0.25%, 0.26% and 0.27 wt%, respectively. That is, the oxidation with 100 ppm during the consolidation of the composite Ti powders by the process as mentioned above slightly occurred. Figure 2 shows XRD patterns of P/M extruded titanium with no CNT and reinforced with 0.35 wt% CNTs. The peaks of in-situ synthesized TiCs of the composite material are obviously detected at $2\theta = 36.08^\circ$, $41.74^\circ$ and $60.89^\circ$ when using titanium powder coated with CNTs as shown in Fig.2 (b). Additionally, there is no difference of $2\theta$ for titanium peaks between extruded Ti and reinforced with CNTs. Figure 3 indicates optical microstructures of P/M extruded pure titanium (a) and reinforced with 0.35 wt% CNTs (b). A mean grain size of the TMC with CNTs and no CNT is around 5μm and 6μm, respectively, and no significant difference between them is observed. However, the former has a lot of small grains less than 3μm and many twins induced inside the grain. It suggests that nanotubes are effective to obstruct the grain growth during heating in SPS and extrusion by their pinning effect and to form the stress concentration causing the twins. Furthermore, no pore is observed in both specimens. The relative density of P/M extruded titanium and reinforced with 0.35 wt% CNTs measured by Archimedes law is 99.91% and 99.87 %, respectively. Both P/M materials are completely consolidated by SPS and hot extrusion process. The optical and scanning electron microscope observation results on extruded TMC with CNTs are shown in Fig. 4. TiC particles are uniformly distributed in the matrix, that is, the original distribution of un-bundled CNTs on Ti powder surface is homogeneous. The image analysis on the optical microstructure of Fig. 4 (a) indicates a mean particle size of in-situ formed TiC is 1.8μm. The TiC dispersoids have two different shapes; elongated and spherical type. Most of the formers, having a length of about 10 $\mu$ m or less, are lined along the extrusion direction because of the severe plastic deformation of the titanium matrix powder and recombination of CNTs during hot extrusion. Then; CNTs are also lined along the direction, and reacted with the titanium matrix, resulting elongated TiCs. The formation of spherical TiC particles indicates the incompletely disassembled CNTs, causing the coarse TiC particles, partially exist on the powder surface even after this wet process. The dark areas around any TiC particle are detected, and the magnified observation by FE-SEM is shown in Fig.4 (b). It is obviously clarified that they correspond to the titanium matrix, and have a good bonding with the TiC particle due to the solid-state reaction in heating at 1273 K. Furthermore, the titanium matrix seems as the porous lamellar structure in perpendicular direction with paper, which is presumed that corroded by hydrous solution during etching. This trend may be due to the effect of TiC particle on the orientation of lamellar structure at interfaces during phase transformation in hot extrusion process.

The tensile test results are shown in Table 1 and Fig.5, showing the stress-strain curves of extruded pure titanium (a) and reinforced with 0.35 wt% CNTs (b). Each value in the bracket [ ] of Table 1 means the difference between maximum and minimum of the measurement. Tensile strength of P/M extruded Ti with no CNT prepared in this study is 591 MPa as UTS, and significantly superior to that of the conventional wrought titanium with 250 MPa [20]. This is due to both the large oxygen content and extremely fine grains. In particular, concerning the grain size, the P/M titanium materials are prepared by using rapidly solidified titanium powder by the atomization process, and show a mean grain size of about 6μm as mentioned above. As shown in Table 1, the mean values of tensile strength, yield stress and micro-Vicker’s hardness increase in proportion to the CNT content. The scattering of TS for three tensile specimens is 9~13 MPa, and very small and reliable. As a remarkably suggested point, in spite of the strength increment, the elongation to failure is about 34~38%, and independent of the content. According to the chemical analysis results of the oxygen content of each specimen, there is an increment of 100 ppm oxygen of TMC with 0.35 wt% CNTs compared to the pure titanium with no CNT. 1 wt% addition of the oxygen content of pure titanium causes the increment of 13.2 MPa TS and 13.6 MPa YS [20]. This means that the effect of the oxygen increment on these TMC materials reinforced with nanotubes is very small. Therefore, the increased TS and YS of the composites are mainly due to the dispersion strengthening effect by un-bundled CNTs and in-situ synthesized TiC fine particles. Furthermore, when adding CNTs to Ti powder, the micro-Vickers hardness value gradually increases from 261 to 285 with increase in the CNT content. Figure 6 shows the fractured surfaces of tensile specimens of pure titanium (a) and reinforced with 0.35 wt% CNTs (b). P/M extruded pure titanium reveals fine dimple patterns, but no primary particle boundaries. This means that the titanium powder bonding is metallurgically good, and the fracture occurs inside the grains when applying SPS and hot extrusion to consolidate titanium powders. As shown in g Fig.6 (b), un-bundled CNTs have been remained in matrix, and keep their original size and shape at the surface of the composite. On the other hand, TiC particles formed by the reaction of CNT with Ti are also obviously observed. It means that solid-state sintering condition at 1073 K by SPS and pre-heating at 1273 K before extrusion are suitable to prepare the Ti composite including both of CNTs and TiC particles, which are effective for improving the mechanical response.

## Conclusions

(1) Wet process using the zwitterionic surfactant solutions was effective to coat un-bundled CNTs on Ti powder surface, and assemble them in P/M extruded titanium composite.

(2) In-situ formed TiC particles were also uniformly distributed in the matrix, and had elongated and spherical shapes.

(3) Mechanical properties of tensile strength and micro-vicker's hardness were remarkably improved by the reinforcement of 0.35 wt% CNTs. In particular, TMC via this process showed a good balance of high UTS of

742 MPa and large elongation of 26% when using pure titanium powder as input raw materials.

(4) Observation on the fractured surface of tensile specimens indicated that CNTs were still remained with no morphological change after SPS and hot extrusion. The nanotubes and in-situ synthesized TiC fine particles presumably promoted the mechanical properties of extruded titanium composites.

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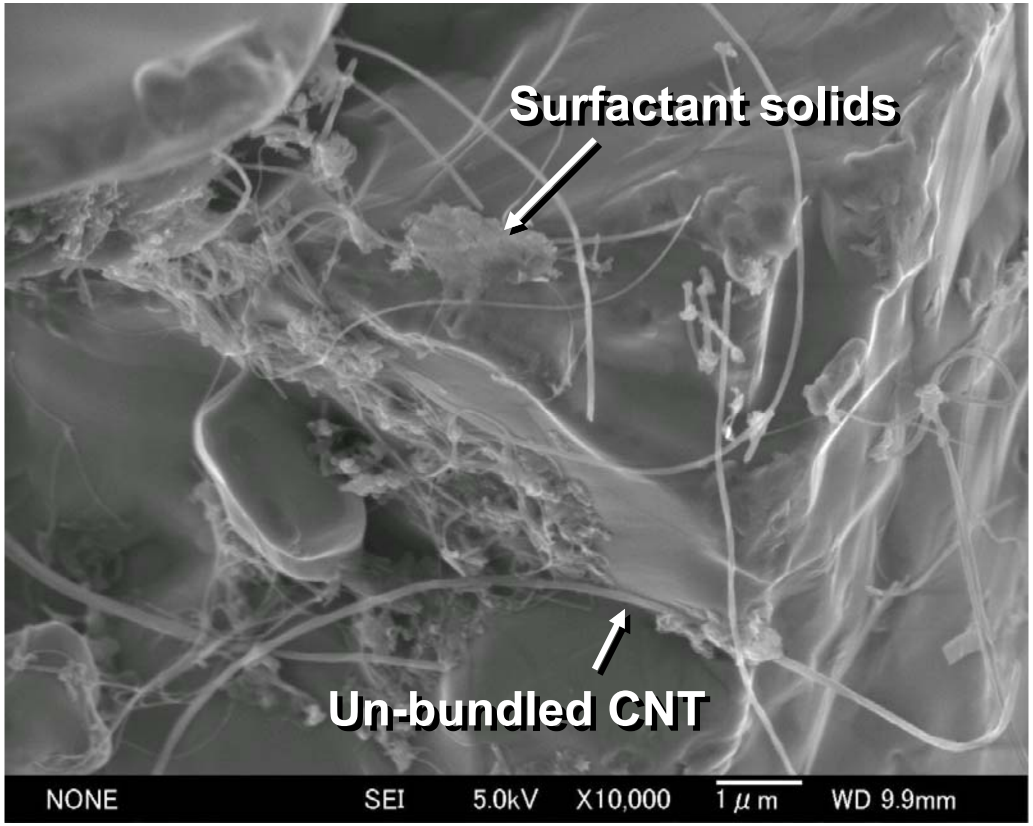


Figure 1: SEM observation on surface of pure titanium powder coated with un-bundled CNTs.

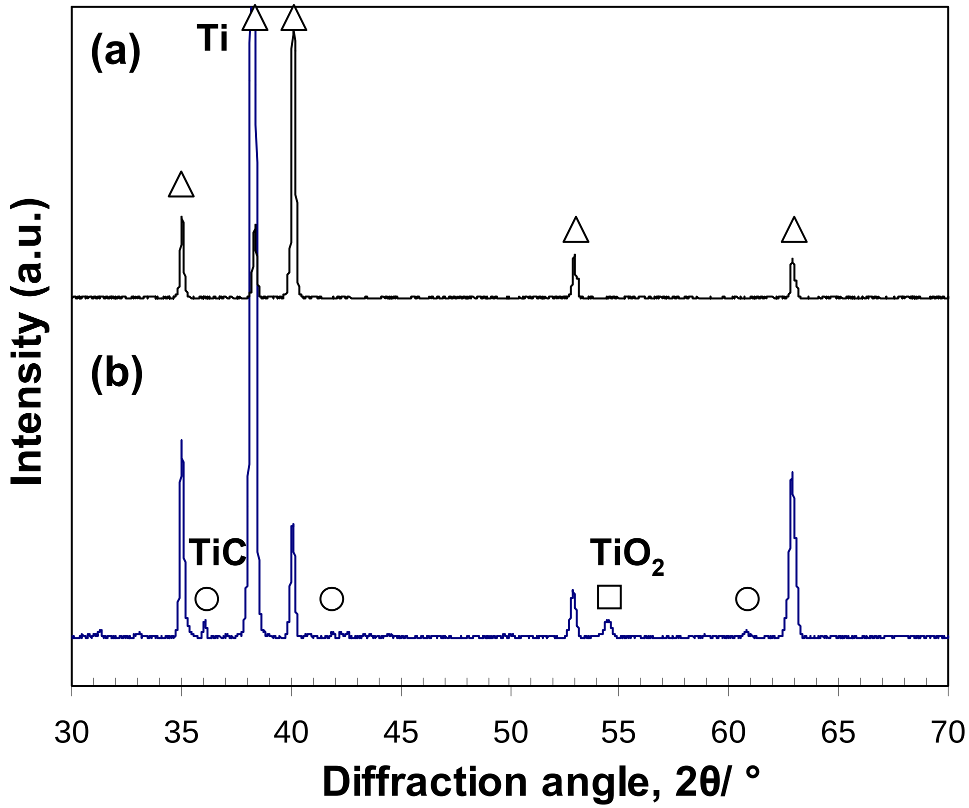


Figure 2: XRD patterns of P/M extruded titanium with no CNT (a) and reinforced with 0.35 wt% CNTs (b).

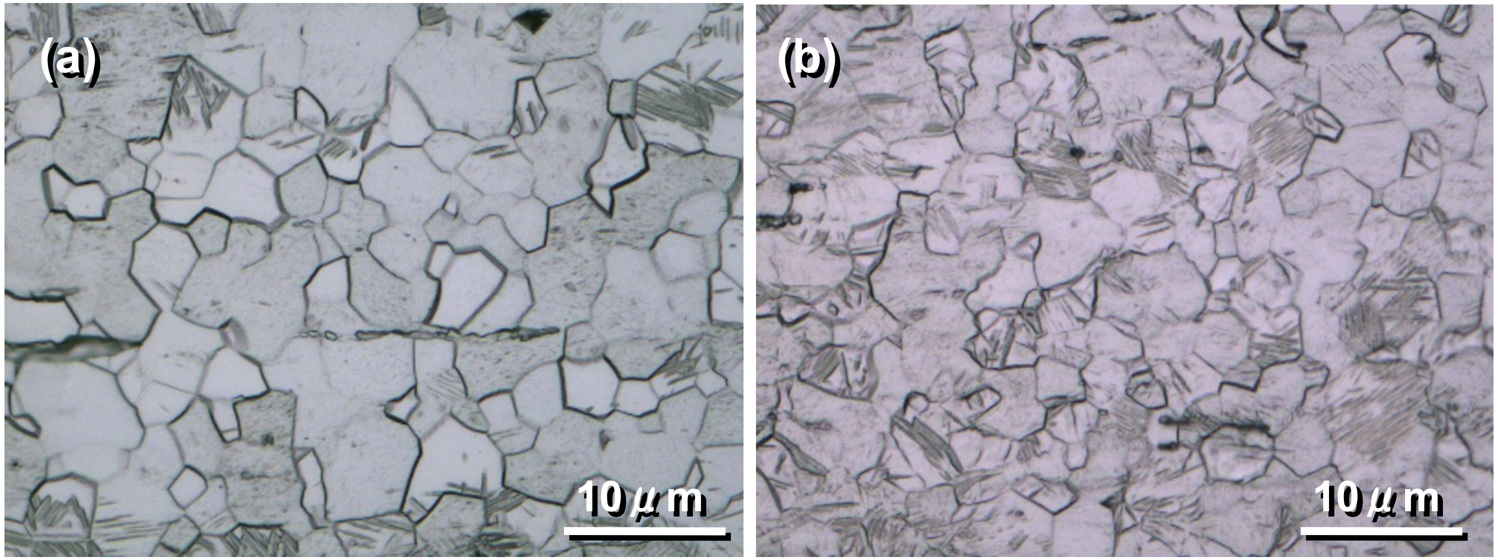


Figure 3: Optical microstructures of extruded titanium with no MWCNT (a) and reinforced with 0.35 wt% MWCNTs (b).

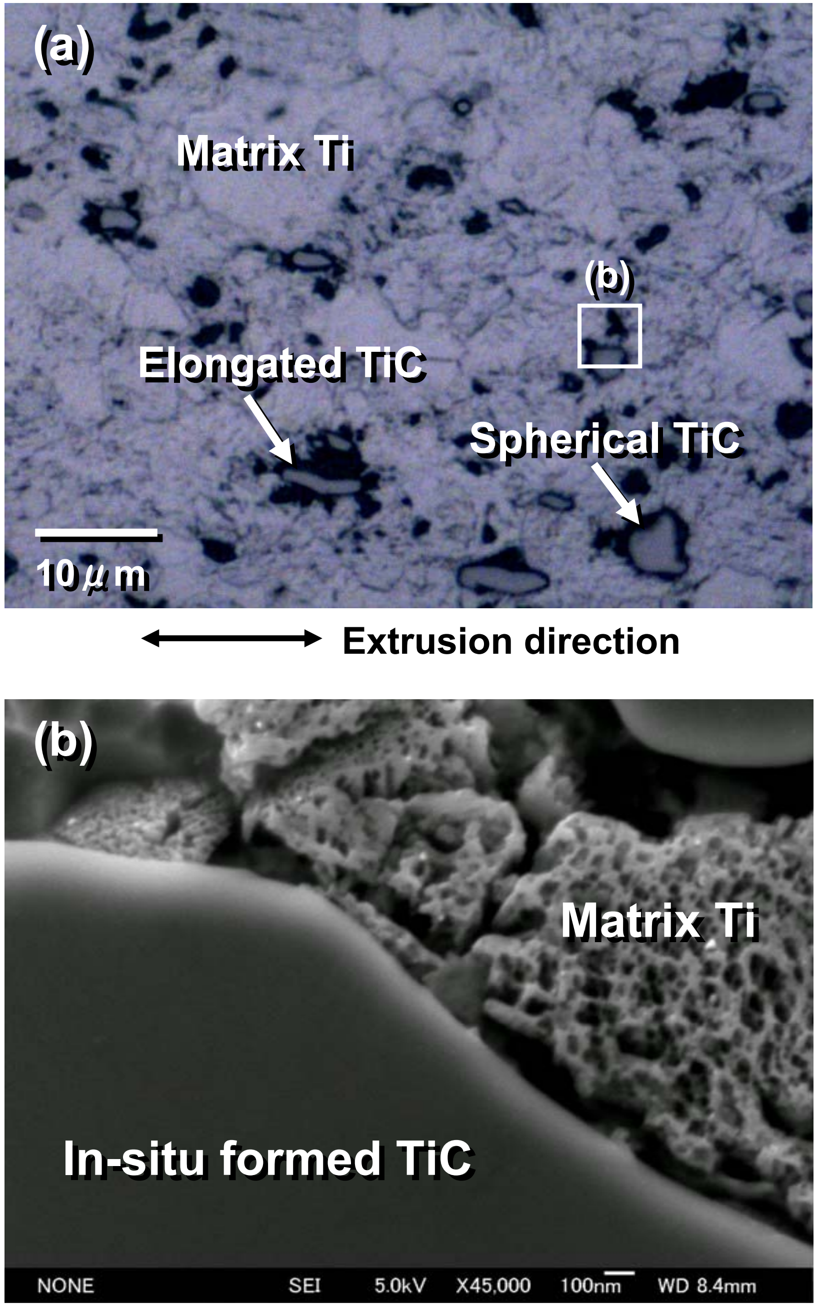


Figure 4: Optical microstructure of P/M extruded TMC with CNTs (a) and interface observation between TiC and titanium matrix (b) observed by scanning electron microscopy.

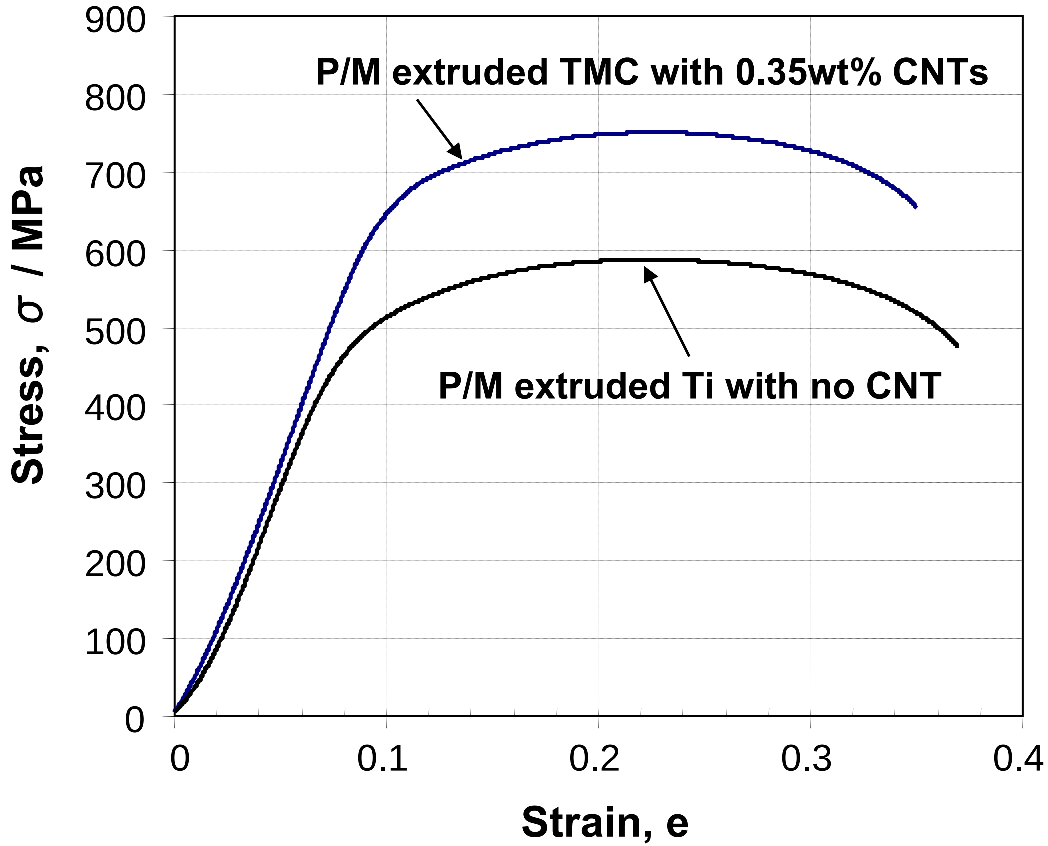


Figure 5: Stress-strain curves of P/M extruded titanium and reinforced with CNTs.

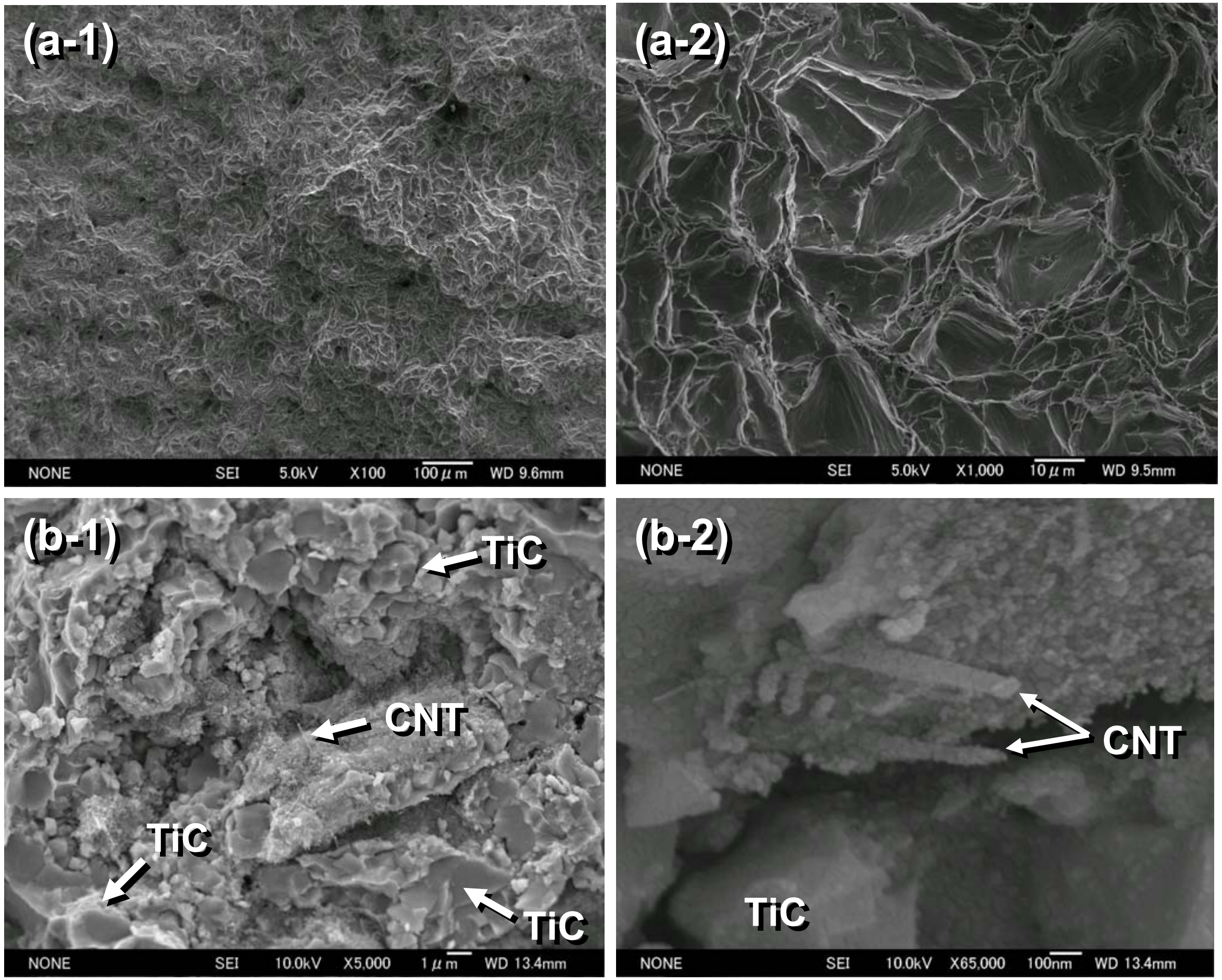


Figure 6: SEM observation on fractured surface of tensile specimen; P/M extruded titanium with no CNT (a) and reinforced with 0.35 wt% MWCNTs (b).

Table 1 Tensile properties and hardness of P/M extruded titanium and reinforced with MWCNTs.

| | TS (MPa) | YS (MPa) | $\varepsilon_f$ (%) | Hv (0.05N) |
|---|---|---|---|---|
| Pure Ti | 591 [9] | 472 [9] | 36.2 [2.1] | 261 |
| +0.18%CNT | 682 [11] | 590 [12] | 34.2 [2.3] | 275 |
| +0.24%CNT | 704 [8] | 633 [10] | 38.1 [1.8] | 278 |
| +0.35%CNT | 754 [10] | 697 [13] | 34.8 [2.4] | 285 |

$\varepsilon_f$ ; elongation to failure, Hv; micro-Vicker’s hardness,
[ ]; maximum-minimum value