

Microstructures and Mechanical Properties of Powder Metallurgy Pure Ti Composite Reinforced with Carbon Nanotubes[†]

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Abstract

Powder metallurgy (P/M) titanium matrix composite (TMC) reinforced with carbon nanotubes (CNTs) was prepared by spark plasma sintering (SPS) and a subsequent hot extrusion process. The un-bundled CNTs were coated on the pure titanium powder surface by the zwitterionic surfactant solution of the wet process. The microstructure and mechanical properties of P/M pure titanium materials and those reinforced with CNTs were evaluated. The microstructure and synthesized compound in solid-state sintering were investigated by optical and scanning electron microscopy equipped with an EDS analyzer. The mechanical properties of TMC were significantly improved by the addition of CNTs. For example, when employing fine pure titanium powder as raw material, P/M titanium extruded material with 0.37mass% showed excellent tensile properties such as 742 MPa UTS, 592 MPa YS and 26% elongation compared to P/M wrought titanium with no CNT having 585 MPa UTS, 423 MPa YS and 30% elongation. Fractured surfaces of tensile specimens were analyzed by scanning electron microscope, and revealed a uniform distribution of CNTs and TiC particles of the composite.

KEY WORDS: (Pure Ti) (Carbon Nanotube) (Hot Extrusion) (TiC)

1. Introduction

Recently, metal matrix composites reinforced with carbon nanotubes (CNTs) have been studied mainly by using powder metallurgy processes because they have a low density of 1.3 g/cm³ and 973 GPa Young's modulus¹⁻³). It is also well known that CNT have excellent characteristics such as high mechanical properties, electrical and thermal conductivities⁴). Various metals were selected as matrices such as aluminum, magnesium and copper⁵⁻⁷). Titanium and titanium alloy are also of interest as the base matrix because they are widely used in various industrial applications, for example, automotive, motorcycles, and airplane industries due to their high specific strength. The chemical and petrochemical applications are also suitable because of their high corrosion resistance⁸). Therefore, it is strongly expected that the combination of titanium (Ti) and CNT will offer superior mechanical properties to the conventional TMC. In this study, the

advanced fabrication process of TMC reinforced with CNTs, based on the wet process to coat the un-bundled CNTs on Ti powder surface by using the zwitterionic surfactant solutions⁹), is explained. The strengthening mechanism of the composites is discussed by investigation of their microstructures analysis and identification of the dispersoids.

2. Experimental

Two different kinds of pure Ti powders, Fine Ti and Sponge Ti, with an average particle size of 30 μm and 686 μm were used as starting materials, respectively. The chemical compositions of the powders are shown in **Table 1**. Oxygen content of fine and sponge Ti powder was 0.21wt.% and 0.069wt.%, respectively. The former includes higher oxygen content because its specific surface is larger than that of sponge Ti powder. Each Ti powder was coated by 3.0wt.% CNT suspension in the zwitterionic surfactant solution via a wet process. Powders were directly dipped in the solution, and

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Table 1 Chemical compositions of raw Ti powders used in this study. (mass %).

	Purity	Fe	Cl	Mg	Si	N	C	O	Ti
Fine Ti	>95	0.03	<0.002	<0.001	0.01	0.02	<0.01	0.21	Bal.
Sponge Ti	>97	0.01	0.07	0.03	<0.01	<0.01	0.01	0.069	Bal.

subsequently dried in an oven at 373 K for 10.8 ks. The coated powders after drying were synthesized into TiC compounds by spark plasma sintering (SPS). In this study, SPS conditions consist of two step sintering under a vacuum atmosphere. The first step was for the surfactant removal by heating at 873 K for 3.6 ks, corresponding with TG result of the surfactant. The second step was TiC synthesis at 1073 K for 1.8 ks in accordance with high-temperature X-ray diffraction (XRD) results detecting the TiC peak. Load for SPS in the two step sintering was 20 kN and 41.6 kN, respectively. Compacts were then heated at 1273 K for 180 s. in argon atmosphere, followed by extrusion. The extrusion ratio, speed and die temperature were 37, 3.0 mm/s and 673 K, respectively. Microstructure and phase characterizations were investigated by XRD, optical and scanning electron microscopy (FE SEM JSM6700) equipped with EDS. The extruded TMCs were machined to tensile specimen bar with 10 mm. gauge length.

3. Results and Discussion

Figure 1 shows the surface of Ti composite powder coated by CNTs, using fine Ti powder (a) and sponge Ti powder (b). In case of fine Ti powders, a few of CNTs are dispersed on the surface, and locally exist on the surface. On the other hand, sponge Ti powders have more uniform distribution of CNTs on the surface than fine Ti powders and tend to accumulate on the facets, as shown in **Fig 1(b)**.

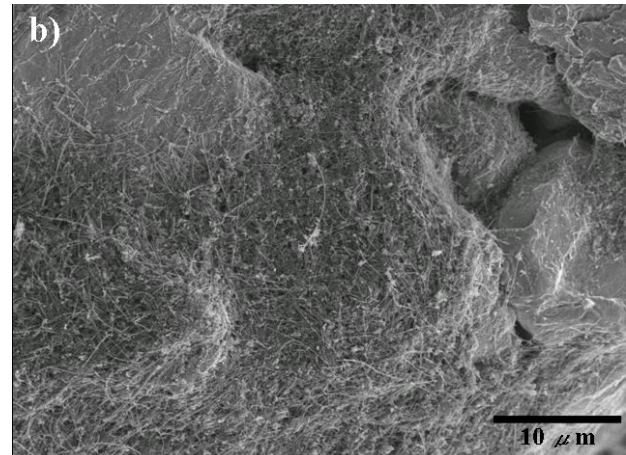
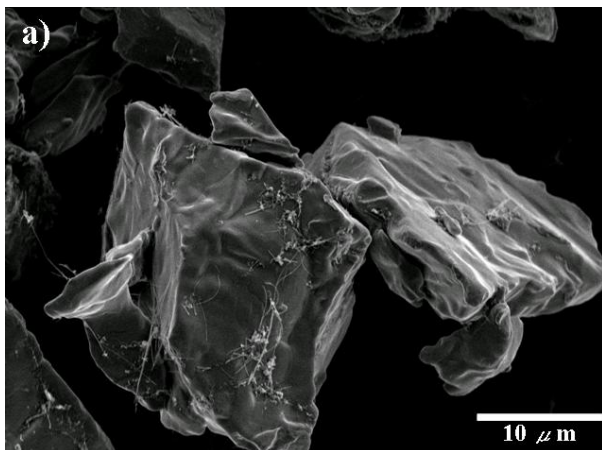


Fig.1 SEM observation of Ti composite powder coated by CNTs; fine Ti powder (a) and sponge Ti powder (b).

X-ray diffraction patterns of the extruded Ti composite with and without CNT are shown in **Fig.2**. The first peak of TiC at $2\theta = 36.08$ and 35.98 , and the second peak at 41.74 and 41.70 degree are detected for the case of fine and sponge Ti/CNT sample, respectively. The high accuracy characterization of TiC structure derived from CNTs will be investigated further. In both composites with CNTs, the oxidation of powders does not occur, that is no TiO_2 is synthesized during consolidation.

The optical microstructures of extruded Ti/CNT composites at 1273 K are shown in **Fig. 3**, where pure fine titanium (a) and pure sponge titanium (b) are used as input raw materials.

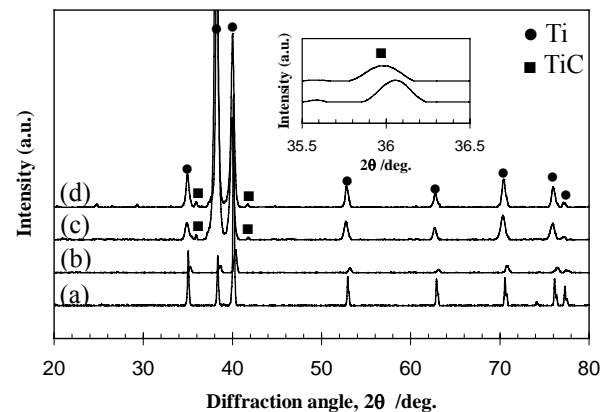


Fig.2 X-Ray diffraction patterns of extruded pure Ti matrix composite; fine Ti (a), sponge Ti (b), fine Ti coated with CNTs (c) and sponge coated with CNTs (d).

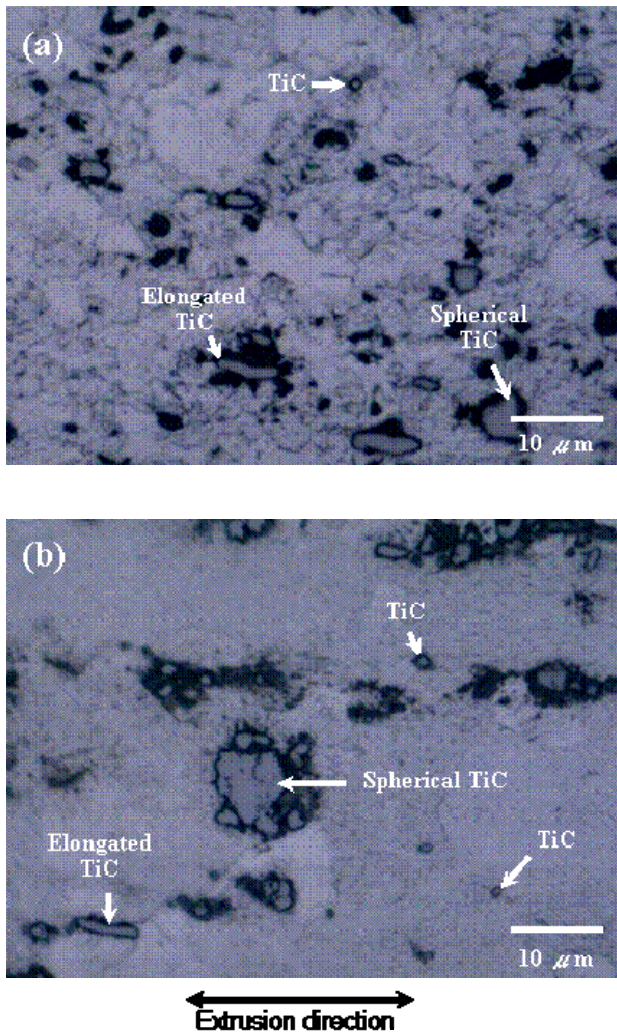


Fig.3 Optical microstructure of extruded pure Ti/CNTs composites by using Ti (a) and sponge Ti powder (b).

P/M titanium extruded material including fine and sponge Ti includes the embedded TiC particles (by arrows) with an average size of 1.8 μm and 2.3 μm , respectively, in the α -Ti matrix. An average grain size of both Ti/CNT composites is $\sim 6 \mu\text{m}$ and $\sim 8 \mu\text{m}$ which are not significant by different from the extruded pure Ti without CNTs at $\sim 4 \mu\text{m}$ and $\sim 5 \mu\text{m}$, respectively. TiC particle shape is mostly elongated along the extrusion direction except for some particles with nearly spherical shape. This feature suggests that many CNTs at facets of powder are recombined during consolidation by hot extrusion process. The dark region around TiC particles corresponds to pure Ti matrix, as shown in the **Fig. 4** SEM photo. This region (arrow in **Fig 4a**) appears as the porous lamellar structure in perpendicular direction with paper, which is presumed to be 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 the hot extrusion process.

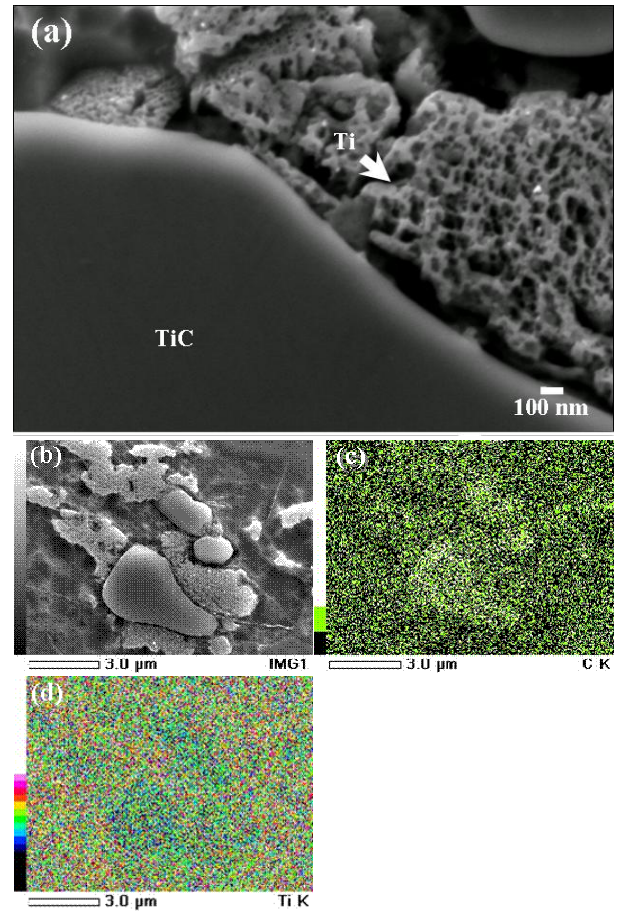


Fig.4 SEM photograph of extruded fine Ti/CNTs composites show, lamellar structure at Ti/TiC interface (arrow) (a), and EDS mapping; SEI image (b), Elemental C (c), Elemental Ti (d).

The extruded TMCs are machined to tensile specimen bars with a gauge length of 10 mm and 3 mm in diameter. The yield stress and UTS values of extruded fine and sponge Ti composite are 592, 367, 742 and 521 MPa, respectively. The yield strength and UTS of fine Ti composite are increased by 39 % and 26%. In case of sponge Ti, the yield strength and UTS is increased by 53 % and 40 %, respectively. The increasing percentage of yield strength and UTS of sponge Ti composite are higher than fine Ti composite which can account for the CNTs content, which is increased from 0.01 wt.% to 0.37 wt.%, and the uniform distribution of CNTs on the powder surface. Elongation percentage of TMC, in case of fine Ti, is not different between extruded composite and pure Ti specimen at values of 25.9 % and 29.7%. The significant difference of elongation, in case of sponge Ti composite, is 19.9 % and 34.4 % for extruded sponge Ti with and without CNTs. When adding CNTs to Ti powder, the micro-Vickers hardness values (HV0.05) increase from 261 to 285, and 171 to 204 for fine Ti and sponge Ti composites, respectively.

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Table 2 Mechanical properties of extruded TMC with and without CNTs.

Extruded specimens	0.2%Yield stress (MPa)	UTS (MPa)	Fracture stress (MPa)	Elongation (%)	Hardness (HV0.05)
Fine Ti	423	585	484	29.7	261
Fine Ti/CNT	592	742	658	25.9	285
Sponge Ti	239	371	234	34.4	171
Sponge Ti/CNT	367	521	490	19.9	204

The mechanical properties results are summarized in **Table 2**. Generally, mechanical properties of pure Ti are affected by alloying elements such as Fe and interstitial atoms, i.e. oxygen, nitrogen and carbon¹⁰. There is no significant difference of Fe impurity content between fine Ti and sponge Ti powders. The oxygen content of extruded TMC materials in using fine Ti and sponge Ti powder is 2700 ppm, and 690 ppm, respectively. Such oxygen content of titanium alloys is not remarkably influential on their mechanical properties. In addition, the increased oxygen content of both materials is 500~600 ppm, that is, very small and no difference between them. This means that oxidation phenomena did not occur during CNT coating, sintering, pre-heating and hot extrusion of Ti powders coated with un-bundled CNTs. Therefore, the effects of impurities of extruded materials, in particular the oxygen content, on the strength are neglected. The obvious increase in tensile strength of the extruded TMC reinforced with CNTs in using fine Ti and sponge Ti powder is 157 MPa and 150 MPa, respectively. There is no significant difference of the increased TS because the former has a carbon content of 0.351 wt.%, which is almost same as that of the latter material of 0.371 wt.%. That is, the above increased tensile strength is due to the dispersion strengthening effect of CNTs and in-situ formed TiC fine particles.

Fractured surfaces of TMC specimens are shown in **Fig 5**. CNTs have remained in the matrix of both fine and sponge Ti as shown in **Fig 5a-b**, and confirmed by EDS analysis in **Fig. 5d**). CNTs with the original size and shape are observed at the surface of the composite. On the other hand, TiC particles formed by the reaction of CNT with Ti are also obviously observed. This 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 CNTs and TiC particles. The remained CNTs presumably improve the mechanical properties of TMC.

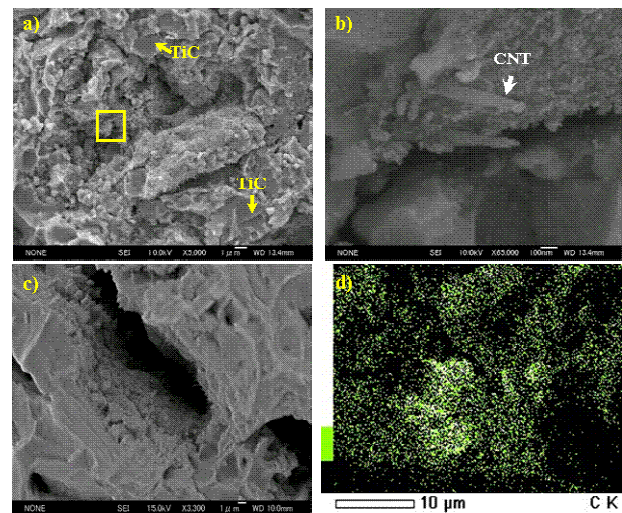


Fig.5 Fractured surfaces of TMC tensile specimen; Fine Ti with CNT (a), High magnification of figure 5a) at the marker (b), Sponge Ti with CNT (c) and EDS mapping image of figure 5c) (d).

4. Conclusions

- (1) Wet process using zwitterionic surfactant solutions was effective in coating un-bundled CNTs on Ti powder.
- (2) CNTs tended to pile on the facets of sponge Ti powder and agglomerate during the hot extrusion process.
- (3) CNT/TiC nano composite particle was synthesized by SPS and hot extrusion process.
- (4) CNTs still remained in the Ti matrix which promoted mechanical properties of pure Ti effectively.

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