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Titanium Matrix Composite Reinforced with In-situ Formed TiC Using Carbon Black Nano Particles via a Wet Process†

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Abstract

Powder metallurgy (P/M) titanium matrix composite (TMC) reinforced with carbon black particles was produced by spark plasma sintering (SPS) and the hot extrusion process. Carbon black particles were added for the in –situ formation of TiC dispersoids in the SPS process. Two kinds of titanium (Ti) powders, sponge and fine Ti, were coated with carbon black particles via a wet process using the zwitterionic solution containing carbon black particles. The distribution of the particles on the Ti powder surface before the consolidation process was observed by scanning electron microscopy (SEM). The morphology and distribution of in-situ TiC phases were investigated by optical microscope and SEM equipped with an EDS analyzer. The mechanical properties of extruded pure Ti composites reinforced with in-situ formed TiC particles were evaluated. The mechanical properties of these composites were remarkably improved by adding a small amount of carbon black from 0.07 ~ 0.16wt.%. Finally, the fractured surfaces of TMC specimens after the tensile test were observed.

KEY WORDS: (Titanium) (Carbon black) (Spark plasma sintering) (Hot compression) (Titanium carbide)

1. Introduction

Titanium and titanium alloys have been drawn interest because they are high specific strength materials and widely used in various industrial applications such as aerospace sectors[1)]. This report shows a simple production method for high strength titanium matrix composites. High strength Ti-based alloys and composites have been fabricated via hot working[2)], ball milling[3-4)] and severe plastic deformation[5-6)] processes but those methods remain the obstacles in the industrial approach, such as the limitation of time, energy consumption, production capability. It has been far from mass production. Recently, Ti reinforced with un-bundled carbon nanotubes (CNTs) via a powder metallurgy route was introduced[7-8)]. One of the researchers in the previous study showed the effective preparation of un-bundled CNTs by using zwitterionic surfactant solutions via a wet process[9)]. Zwitterionic surfactant, 3-(N,N-dimethylstearylammonio) propanesulfonate, was used in this study. The electrostatic interaction between positive and negative charges of hydrophilic groups is attracted together, while the neutral charge of the hydrophobic group is attracted to the surface of carbon nanotubes. The successful application of the above wet process on pure titanium reinforced with multi-wall carbon nanotubes are described elsewhere[7-8)]. By using the same mechanism, the uniform distribution of nano-particulates by the typical linear zwitterionic surfactant solution is applied to carbon black nano-particles. In the present study, the commercially pure titanium powders coated with non-agglomerated carbon black particles were prepared by the wet process, and consolidated by SPS and hot extrusion as wrought composites. It was concluded that the application of the wet process to carbon black nano-particles conferred superior mechanical properties for P/M titanium matrix composites reinforced with in-situ formed TiC dispersoids.

2. Experimental

Two kinds of commercially pure Ti powder, sponge and atomized Ti powders, having a mean particle sizes of

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686 μm and 30 μm, were used as the starting materials, respectively. The chemical compositions of the starting materials are shown in **Table 1**. Carbon black (CB) particles with an average diameter of 290 nm were used as the reinforcement. This is because CB particles are very cheap materials compared to carbon nanotubes, and useful for synthesizing titanium carbide (TiC) particles via the SHS process[10]. A typical linear zwitterionic surfactant solution with carbon black concentration of 0.5 wt.% was prepared. Ti powders were immersed into the aqueous carbon black/zwitterionic solution, and subsequently dried in an oven at 373 K for 10.8 ks. Ti powders coated with carbon black particles were obtain. The solid surfactants also exist on the Ti surface, and should be eliminated before the consolidation process because they changed to gases at elevated temperature over 773K [11], creating pore defects in bulk consolidated materials. To eliminate the solid zwitterionic substance, the coated Ti powders were heated again in a horizontal tube furnace at 873 K for 3.6 ks under an Ar gas atmosphere. The composite Ti powders with CB particles were consolidated by a spark plasma sintering (SPS, Syntech Co. SPS-103S) process at 1073 K for 1.8 ks under vacuum atmosphere. The applied load during the process was 30 MPa. The sintered Ti billet was heated to 1273 K for 180 s under an Ar atmosphere, and immediately transferred to the hot extrusion process. The extrusion ratio, speed and die temperature were 37, 3.0 mm/s and 673 K, respectively. Microstructure and phase characterization of extruded Ti composites were investigated by X-ray diffraction (XRD, Shimadzu XRD-6100), optical microscope and scanning electron microscope equipped with an energy dispersive spectrometry (SEM-EDS, JOEL, JSM-6500F). The extruded Ti composite materials were machined to tensile specimen bars with 3.0mm-diameter and 20mm-gauge length. The mechanical properties were evaluated by universal test machine (Autograph AG-X 50kN, Shimadzu) under a strain rate of 5×10^{-4} /s. Hardness was measured by a micro-Vickers hardness tester (Mitutoyo). The fractured surfaces of tensile specimens were observed by SEM.

3. Results and Discussion

Figure 1 shows SEM photo showing the appearance of carbon black particles used as raw materials in this experiment. The irregular shape carbon black particles have an average size of 290 nm. They consist of the agglomerated primary particles, having a mean size of 100 nm or less. **Figure 2** shows the appearance of Ti powders coated with CB particles. The local surface of Ti powders was covered with CB particles because the concentration of CB was 0.5wt.% and not enough to fabricate the completely coated Ti/CB composite powders. The solid surfactants also existed on the Ti surfaces, shown by arrows, and should be eliminated before consolidation process. Most of the CB particles are locally deposited on the curve of powders.

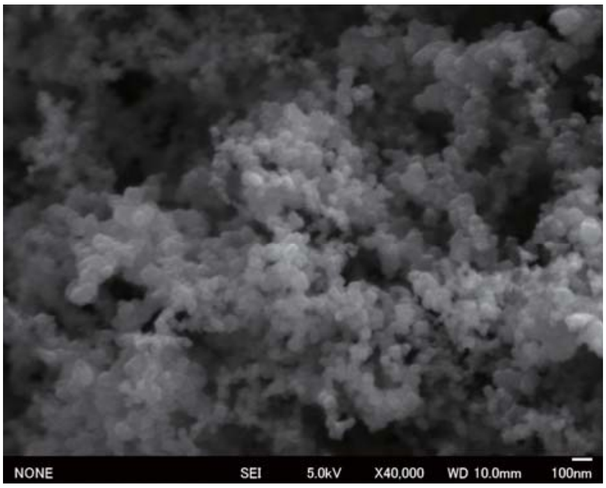

Fig.1 SEM image of the carbon black particles used in this experiment.

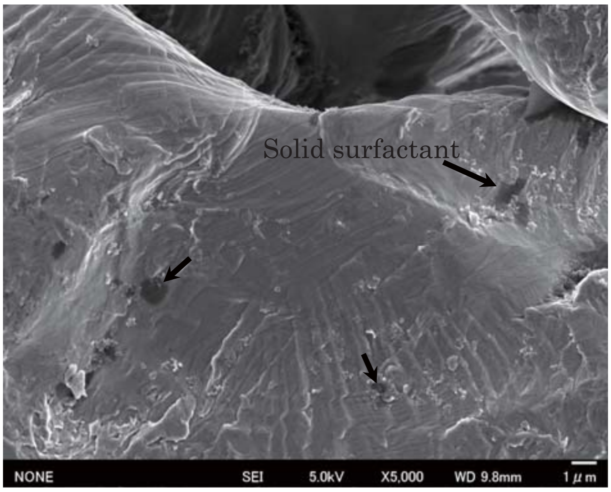

Fig.2 Ti powder coated with carbon black particles via a wet process.

After elimination of the solid zwitterionic substance at 873 K for 3.6 ks, the Ti powders had partially reacted with CB to form TiC at the interface as shown in **Fig.3**, which is consistent with theoretical thermodynamics and experimental data [12-15].

X-ray diffraction patterns of the extruded Ti composite materials reinforced with in-situ formed TiC composite are shown in **Fig.4**. The first peaks of TiC at 2θ = 35.74 and 36.04 deg. are detected in both extruded sponge and fine Ti/CB samples. The second peak is, however, detected at 41.72 deg. for fine Ti sample only. The relative intensity and the breadth of the TiC peak of extruded fine Ti/TiC composite obviously indicated that the volume fraction and size of TiC particles have very small existences in the matrix. TiO_2 peaks could not be detected in this study which means the oxidation does not occur inside the extruded materials during hot extrusion process, and does not affect the mechanical properties.

Table 1 Ti powder coated with carbon black particles via a wet process.

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

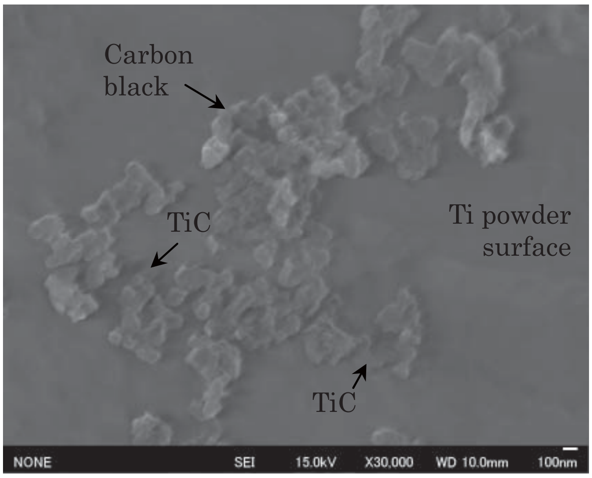

Fig.3 Partial bonding of Ti/carbon black after annealing at 873K for 3.6 ks

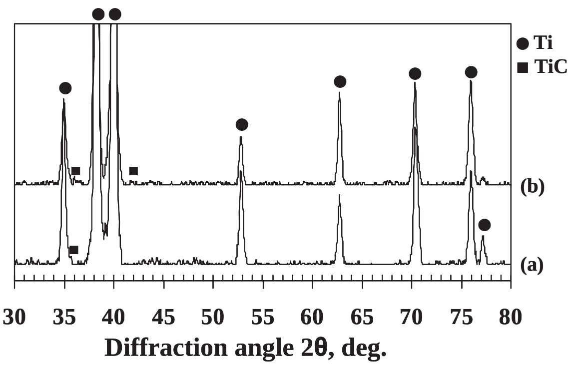

Fig.4 XRD patterns of extruded sponge (a) and extruded fine Ti composites (b) with in-situ formed TiC

Microstructures of extruded Ti/CB composites are shown in **Fig.5.** TiC particles are uniformly distributed in the matrix as shown in **Fig. 5** (a) and (c), which explains the high distribution of CB particles on Ti powder surface by the wet process. The particle size measurement of both sponge and fine extruded Ti/CB composites indicates that the size of in-situ formed TiC is 1.8 and 3.0 μm, respectively. The grain size measurement of extruded Ti composites with CB and without CB reinforcement indicates the grain size in the range of 4 to 7 μm. The grain size of all extruded samples has not significant difference between them. Therefore, the effect of grain size on mechanical properties will be the same level, and does not show an important role higher than those of in-situ TiC dispersiods. An average grain size and TiC particle size of all extruded samples are summarized in **Table 2**.

The tensile test results are shown in **Fig.6**, revealing stress – strain curves, and summarized in **Table 2**. Tensile properties of extruded Ti without CB prepared in this study are almost same as those of the conventional pure Ti [16-17]. The average yield stress (YS) and tensile strength (TS) values of extruded sponge and fine Ti/TiC composites are 317, 479, 744 and 878 MPa, respectively. In the case of sponge Ti powders, the increment of YS and TS by adding CB particles are 28.3% and 16.2%, respectively. In the case of extruded fine Ti/TiC composite, YS and TS are significantly increased 64.2% and 35.7%, respectively. The increasing percentage of YS and TS of sponge Ti composite is due to the increment of carbon content, which is increased from 0.01 to 0.073 and 0.162wt.% for sponge and fine Ti, respectively.

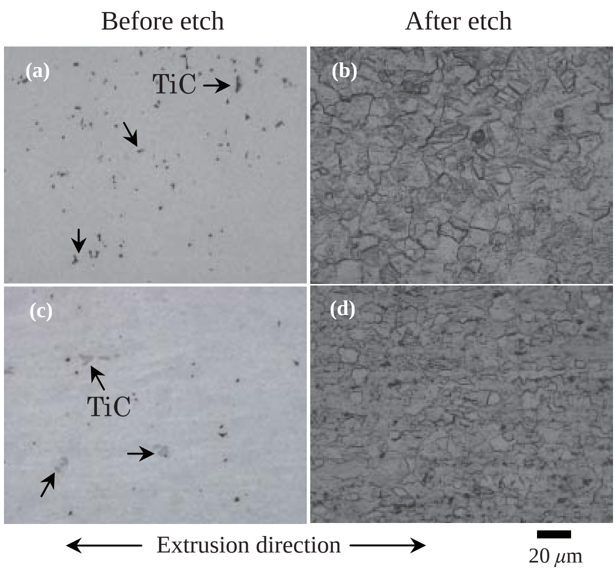

Fig.5 Optical microstructures of P/M extruded titanium composite reinforced with TiC dispersoids using sponge Ti/carbon black (a)-(b) and fine Ti/carbon black (c)-(d)

The dispersion of in-situ formed TiC particles in the matrix caused an enhancement of mechanical properties of Ti/TiC composites. Elongation percentage of the extruded sponge and fine Ti/TiC composite is decreased 7.87% and 21.45%, compared with the extruded pure Ti composite with no reinforcement.

Table 2 Mechanical properties of extruded titanium reinforced with TiC particles

Samples	Grain size (μm)	TiC size (μm)	E (GPa)	YS (MPa)	TS (MPa)	e_f (%)	HV
Sponge Ti	5.0	-	108	247	412	25.4	171
Sponge/TiC	7.1	1.8	96	317	479	23.4	228
Fine Ti	4.1	-	107	453	647	37.3	261
Fine Ti /TiC	5.3	3.0	116	744	878	29.3	340
Ti-6Al-4V [17)]	-	-	110-140	800-1100	900-1200	13-16	300-400

The micro-Vickers hardness values (HV0.05) increase 33.3% and 30.2% for sponge and fine Ti composites, respectively. The comparison of mechanical properties of fine Ti/TiC composite and conventional Ti-6Al-4V (Ti64) alloy is tabulated in the **Table 2**. By adding a small amount of CB particles, the yield stress and tensile strength of fine Ti/TiC had increased close to those of lower levels of Ti64 alloy. At the same time, the elongation was much higher than that of Ti64 alloy. It is expected that fine Ti/CB composite will replace the conventional Ti64 alloy in the near future.

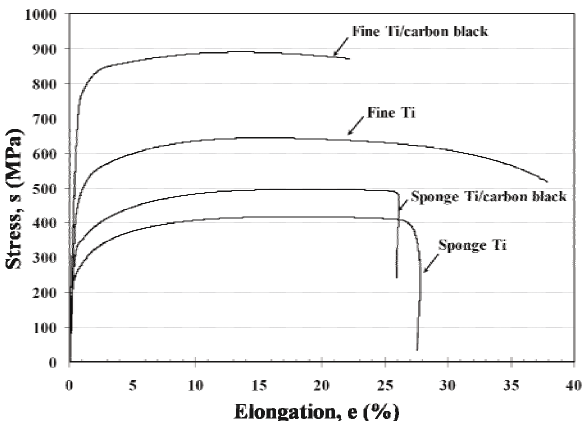

Fig.6 Stress – strain curves of P/M extruded titanium composites reinforced with TiC particles.

The fractured surface of a tensile specimen of sponge Ti/CB composite is selected to be a representative sample. Even $MgCl_2$ and TiFe compounds could not detected by XRD, but the EDS analysis of the fractured surface showed the existence of those defects clearly as shown in **Fig.7**. On the other hand, $MgCl_2$ and TiFe compounds do not present themselves in the case of the fine Ti/TiC composite. The formation mechanism of those defects is still unknown because there are many impurity elements in Ti powders as shown in **Table 1**, and by product of zwitterionic solution after the elimination process. It is believed that the formation of $MgCl_2$ occurred during consolidation by SPS. Mg and Cl atoms have enough time to diffuse and form to be a defect in the matrix, resulting in reduction of the mechanical properties. This is seems to be a characteristic of sponge Ti.

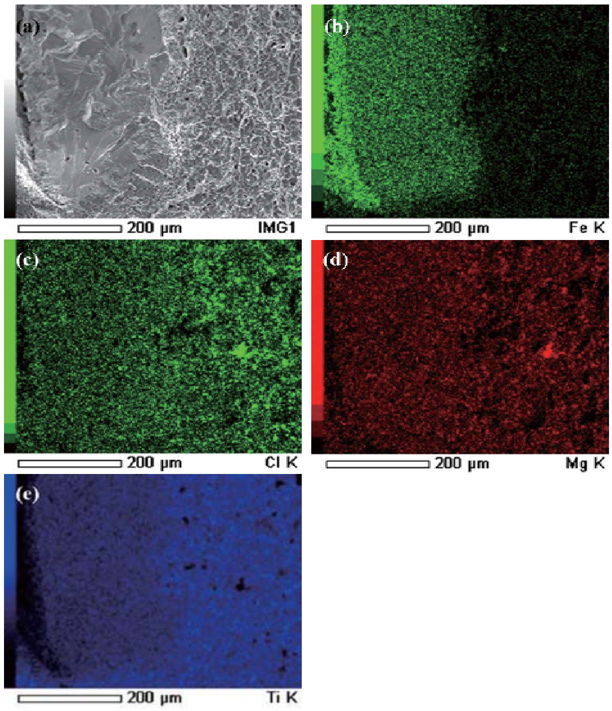

Fig.7 Fractured surface of sponge Ti/carbon black composite: SEI (a) and EDS mapping image of Fe (b), Cl (c), Mg (d) and Ti (e)

4. Conclusions

In this study, the mechanical investigation shows that a very high yield strength of 744 MPa and ultimate strength of 878 MPa as well as considerable ductility (elongation to failure of 29.3%) can be attained in commercially pure Ti by a combination of wet process, spark plasma sintering and hot extrusion. The conclusions of this study are as follows.

(1) Wet process using the zwitterionic surfactant solution was effective for uniformly coating non-segregated carbon black particles on Ti powders surface.

(2) The results of mechanical evaluation revealed that the distribution of in-situ formed TiC particles leads to an improvement in yield strength, tensile strength and hardness of commercially pure Ti powders. The ductility of these composites was adversely affected.

(3) In the case of extruded sponge Ti, the fractured surface of tensile specimens revealed that the main defects were $MgCl_2$ and TiFe which reduce the

mechanical properties of extruded titanium composite. These resulted from the initial content of impurity in the starting materials.

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