Microstructural and Mechanical Properties of Ti Composite Reinforced with TiO_2 Additive Particles†

YOSHIMURA Tomohiro*, THOTSAPHON Threrujirapapong*, IMAI Hisashi** and KONDOH Katsuyoshi***

Abstract

Titanium (Ti) alloys can be applied to various products in aircraft, automotive and motor cycles industries because of their weight reduction effects, superior mechanical responses and high corrosion resistance. Ti-6Al-4V (Ti64) is one of the most common Ti alloys used in structural components. It shows a high tensile strength of 900MPa or more. On the other hand, the poor elongation of about 10% is one of the disadvantages of Ti64 alloys. In addition, high cost additional elements such as vanadium and difficult melting processes increase the total material cost of Ti64. That is why its applications are limited to high-performance products.

In this study, a highly strengthened pure titanium has been developed using high-purity titanium powder (HP-Ti) by elemental mixing with titanium oxide (TiO_2) powder and avoiding the melting process. The main strengthening mechanism of this material is the oxide dispersion strengthening (ODS) by elementally mixed TiO_2 in fine dispersoids. Elementally mixed powder of HP-Ti and TiO_2 was consolidated by the spark plasma sintering (SPS) process. To improve the ductility of sintered material, hot extrusion was applied to sintered HP-Ti. For example, the extruded HP-Ti mixed with 0.8wt% of TiO_2 particles indicated a high tensile strength of 863MPa and good elongation of 26.7%.

KEY WORDS: (Titanium) (Oxide dispersion strengthening) (Spark plasma sintering) (Hot extrusion)

1.Introduction

Titanium based materials are widely used in aerospace, automotives, biomedical and marine applications because of their superior properties, e.g. light weight, excellent mechanical strength and good corrosion resistance[1)]. Ti-6Al-4V (Ti64) is the most typical Titanium alloy, and it is applied in many industrial sectors. Ti64 has an excellent tensile strength of 900MPa or more. However, its application is limited because of the low ductility, poor formability and high material cost. From the view point of cost reduction of titanium alloys, cheaper alloying elements are used instead of the rare earth metals such as vanadium (V)[2,3)]. In addition, aluminum (Al) can be replaced by other low cost elements such as oxygen (O) or nitrogen (N)[4)]. However, this needs an immense amount of energy and special equipment for the melting process of titanium alloy because of its high melting temperature and easy reactivity.

The use of continuous fiber reinforcements is one of the popular methods to improve the mechanical properties of titanium. Silicon carbide (SiC) fibers have been used to reinforce Ti alloys. It is also greatly effective in improving the high temperature strength and creep properties of titanium[5-7)]. On the other hand, the addition of the expensive SiC fibers increases the total material cost. In addition, the large difference of coefficients of thermal expansion between fiber and matrix cause residual thermal stresses. These drawbacks limit the application of SiC fiber reinforced titanium[8)].

Dispersion strengthening is another method to obtain excellent mechanical properties of titanium. There are many kind of dispersoids, i.e. whiskers, intermetallic compounds or ceramics[9-11)]. In general, *in-situ* formed hard and fine dispersoids are effective for improving the mechanical responses of the composite materials, compared to those produced via traditional mixing processes. Therefore, *in-situ* formation of strengthening particles has been drawing interest in recent years, and its mechanical properties are often investigated[12,13)]. In addition, the use of *in-situ* TiC formation by using cheap carbon black fine particles and the powder metallurgy (P/M) method resulted in a good balance of high tensile

† Received on December 18, 2009
* Graduate Student
** Specially Appointed Researcher
*** Professor

Transactions of JWRI is published by Joining and Welding Research Institute of Osaka University, Ibaraki, Osaka 567-0047, Japan.

strength and elongation[14]. The use of *in-situ* formed particles is expected to improve the strengthening effect without remarkable increases in material cost by avoiding the use of expensive alloying elements.

In previous studies, pure titanium was employed as a starting material, and different strengthening mechanisms without any alloying elements were investigated. For example, pure titanium with ultrafine grain structures fabricated via equal channel angular pressing (ECAP)[15,16] or high pressure torsion (HPT)[17] showed grain sizes less than 500nm, and superior tensile strengths of 1200MPa or more[18]. This indicates that extreme grain refinement by applying solid state processing is effective in improving the mechanical response of pure titanium.

In the author's past study, *in-situ* formed titanium oxide (TiO_2) dispersion strengthening and grain refining were applied to improve the mechanical properties of pure titanium. The obtained material had the mean grain size of 6.51μm and oxygen content of 2400ppm. It showed a good balance of tensile strength of 640MPa and elongation of 17.2%[19], but the strengthening effect of grain refinement was not so large. That is because its grain size was larger than 5μm, which was too large to obtain enough strengthening effect. In addition, obtaining bulk material with sub-micron microstructure needs some complicated processes. Compared with that, ODS material is much easier way to make the bulk material, and very effective for improving the mechanical properties of pure titanium.

In the present study, high-purity (HP) Ti powder was employed as a starting material, and TiO_2 particles were used as reinforcements. TiO_2 powder was elementally mixed with HP-Ti powder. The mixed powder was sintered by the spark plasma sintering (SPS) process, and its compact was consolidated into full density by hot extrusion. Mechanical properties and microstructural observations were applied to the wrought composite materials.

2. Experimental procedure

An elemental mixing process of HP-Ti powder and TiO_2 particles was employed to obtain ODS HP-Ti powder materials. Scanning electron microscope (SEM) observation images of HP-Ti powder, TiO_2 particles and elementally mixed powder are indicated in **Fig. 1 (a), (b) and (c)**. The mean particle size of HP-Ti powder and TiO_2 particles is 28μm and 0.45μm, respectively. These powders were mixed with the percentage of TiO_2 of 0, 0.2, 0.4, 0.6 and 0.8 (wt%). They were mixed by table ball milling (TBM) equipment. In the process of mixing, a low revolution speed of 90rpm was applied. After 7.2ks milling treatment, it was checked whether they were completely mixed or not by visual observation. When the aggregate of TiO_2 particles were observed, the additional mixing treatment with a few amount of zirconia balls was applied until the aggregate becomes invisible. SEM observation images of mixed powder containing 0.8wt% TiO_2 particles is shown in **Fig. 1 (c)**. The dispersed TiO_2 particles are indicated by arrows on the surface of HP-Ti powder.

Completely mixed powder was sintered by SPS at 1073K for 1.8ks in a vacuum atmosphere. The applied pressure was 30MPa. Sintered compacts, having 42mm diameter and 97～98% relative density, were heated at 1273K for 180s in Ar gas, and immediately consolidated by hot extrusion. The extrusion ratio of 37 was used, and extruded rods of 7mm diameter were obtained. Tensile test specimens were machined from the extruded rods, and were evaluated under a strain rate of 5×10^{-4}/s.

Specimens for microstructural observation by optical microscope (OM) and SEM were prepared as follows; first, specimens were ground using emery paper of 4000 grit, and next, polished using alumina (Al_2O_3) fine particles solution. Before observation, the polished surface was treated by etching solution.

3. Results and discussions

Figure 2 shows the morphological changes of HP-Ti powder extruded materials with TiO_2 additions. The mean grain size of each extruded material is indicated at the left lower corner of image. It shows that the addition of TiO_2 particles affects the grain size. The grains become finer with the increase of TiO_2 content. This is because the dispersed TiO_2 particles exert the pinning effect of Ti grains during SPS process.

Oxide dispersion morphology was observed by SEM and the obtained images are shown in **Fig. 3**. Many needle-like white dispersoids are obviously detected in the matrix of both oxide additional ratios. High magnification images are shown in **Fig. 3 (c) and (d)**. In the case of 0.8wt% TiO_2 contents, there are many small white dispersed particles which are indicated by white arrows in the image **(d)**. On the other hand, there are almost no white particles in the case of 0wt% TiO_2 content. The needle-like dispersoids and small particles are titanium oxide. This is confirmed by a peak of TiO_2 detected in all X-ray diffraction analysis (XRD) patterns of TiO_2 concentrations, including 0wt%. In conclusion, the small TiO_2 dispersoids are due to admixture of TiO_2 particles, and the needle-like TiO_2 particles are generated by natural oxidation during mixing process by using TBM equipment.

Figure 4 shows the dependence of micro Vicker's

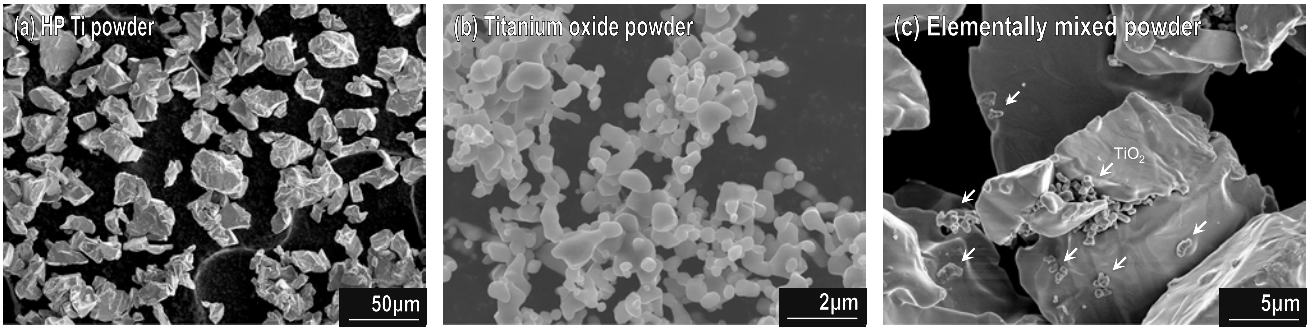

Fig. 1 SEM observation to reveal the powder shape and mixing morphology of HP-Ti powder and TiO_2 particles. (a) HP-Ti powder (raw Material), (b) TiO_2 particles and (c) after mixed powder.

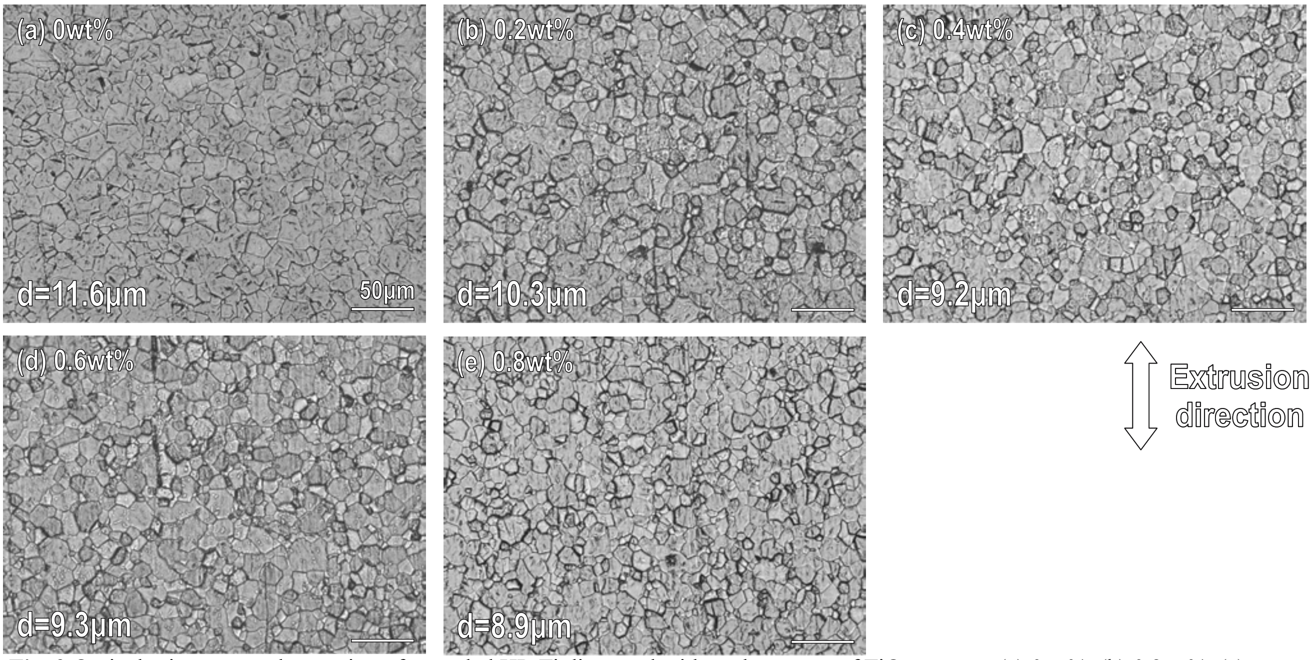

Fig. 2 Optical microscope observation of extruded HP-Ti dispersed with each amount of TiO_2 content. (a) 0wt%, (b) 0.2wt%, (c) 0.4wt%, (d) 0.6wt% and (e) 0.8wt%.

hardness of extruded Ti materials on the amount of TiO_2 content. It becomes larger with increasing TiO_2 additive content, and mostly proportional to its content. The hardening ratio of HP-Ti with ODS material is shown to be 192Hv./TiO_2(wt%). This indicates that the elemental mixture of titanium powder and TiO_2 fine particles is effective for improving the hardness of pure titanium.

Stress-strain curves of tensile test results are shown in **Fig. 5**. Three specimens were prepared from each extruded rod. Their work-hardening behaviors are very similar to each other. **Figure 6** shows the average tensile properties of each extruded rod and dependence of its properties on TiO_2 content. It shows that the 0.2%YS and UTS are obviously improved with increase of the TiO_2 content. For example, the specimen containing 0.8wt% TiO_2 shows excellent 0.2%YS of 703MPa and UTS of 863MPa. In addition, the elongation over 25% was obtained in spite of the remarkable increase of its tensile strength.

To understand the strengthening effect of dispersed TiO_2 particles, it is necessary to consider the effect of Ti grain refinement. As mentioned above, the grain size of powder extruded material reinforced with TiO_2 particles becomes smaller than that of Ti material with no TiO_2. The grain size effects on the 0.2%YS is well known through the Hall-Petch equation[20,21)]. The coefficient of the relationship between the grain size and 0.2%YS of the conventional pure titanium is reported as 18MPa/$mm^{-1/2}$ [22)]. Strengthening due to grain refinement is calculated by that coefficient value and grain size of extruded material, and omitted from the 0.2%YS of extruded HP-Ti via elementally mixing process. The calculated 0.2%YS are shown in **Fig.7**. Closed marks indicate the experimantal measurement of 0.2%YS, and opened marks mean modified values of 0.2%YS by omitting the strengthening amount of grain refinement. It is concluded that the strengthening effect of dispersed TiO_2 particle is indicated as 275MPa/TiO_2(wt%).

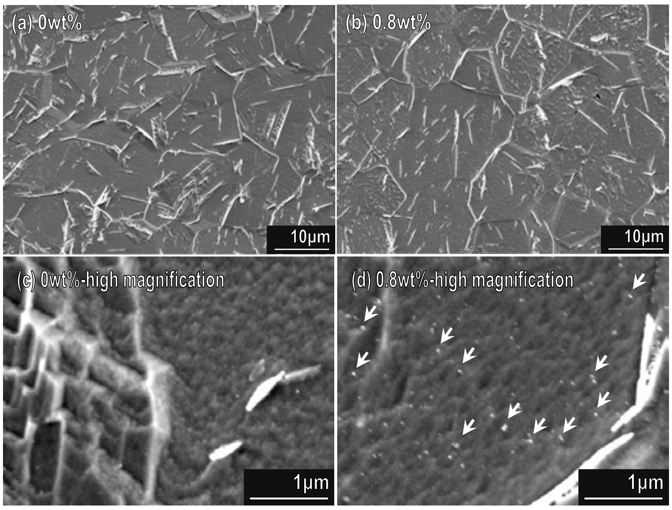

Fig. 3 SEM observation of extruded HP-Ti material reinforced with 0wt% (a) and 0.8wt% (b) TiO_2 particles.

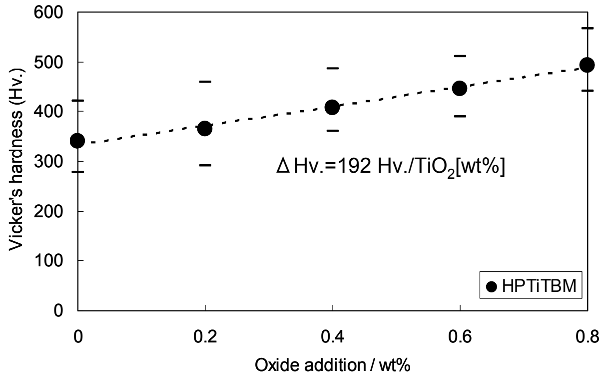

Fig. 4 Dependence of micro Vicker's hardness on TiO_2 concentration of powder extruded specimen via elementally mixing process.

4. Conclusion

The elementally mixing process of HP-Ti powder and TiO_2 particles was used to fabricate highly strengthened pure titanium materials with a cost effect by using cheap TiO_2 particles. The conclusions in this study are as follows;

1. Elemental mixing process was remarkably effective for providing a uniformly mixed powder, and resulted in the uniform dispersion of TiO_2 particles in the matrix of wrought Ti materials.
2. Micro vicker's hardness of powder extruded material was improved by dispersed fine TiO_2 particles, and the hardening ratio was shown as 192Hv./TiO_2(wt%).
3. TiO_2 dispersion strengthening effect by elemental mixture of TiO_2 particles and titanium powder was effective for improving the tensile properties of the extruded pure Ti powder material, and its strengthening effect on 0.2%YS was calculated as 275MPa/TiO_2(wt%).

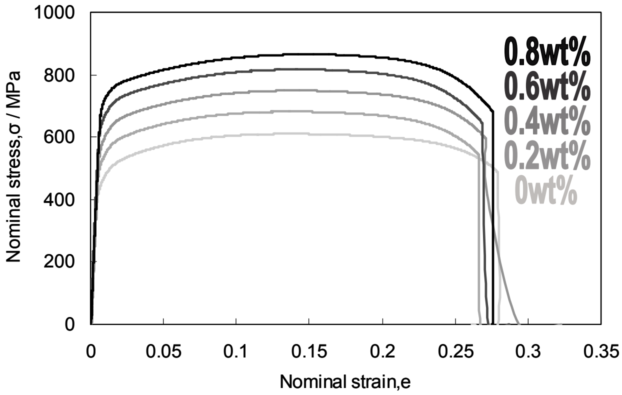

Fig. 5 Typical stress-strain curves of extruded HP-Ti materials including various TiO_2 contents via elementally mixing process.

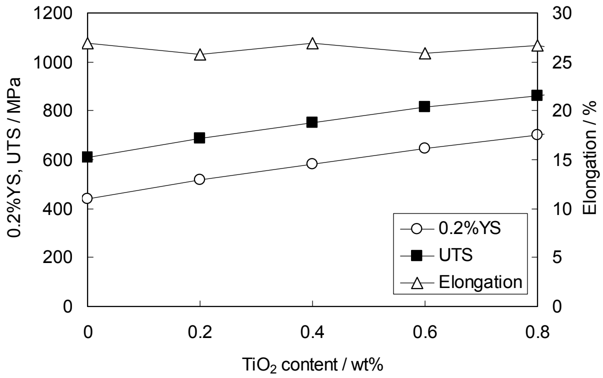

Fig. 6 Average tensile properties of extruded HP-Ti materials reinforced with TiO_2 particles via elementally mixing process.

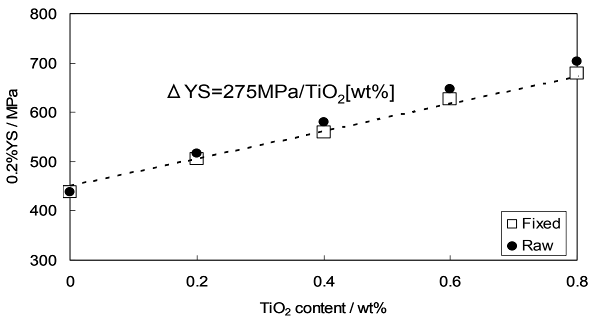

Fig. 7 Dependence of 0.2%YS on TiO_2 content without strengthening by grain refinement.

4. Elongation showed no significant decrease while YS and UTS increased remarkably with increase of TiO_2 additives.

References

1) E. W. Collings: Materials Properties Handbook, Titanium Alloys. Materials Park, OH : ASM International, 1994.
2) P. J. Bania, A. J. Hutt, R. E. Adams and W. m. Parris, Titanium '92 science and technology, ed. By F. H. Froes and K. L. Caplan, (TMS 1993) pp. 2787-2794.
3) P.J. Bania, Beta titanium alloys in the 1990's, ed. By K. Eylon, R. R. Boyer and D. A. Koss, (TMS Materials Park,

1993) pp.3-14.
4) H. Hujii, S. Soeda, M. Hanaki and H. Okano, Titanium ’95, ed. By P. A. Blenkinsop, W. J. Evans and H. M. Flowder, (IoM, London. 1995).
5) D. Bettge, B. Günther, W. Wedell, P. D. Portella, J. Hemptenmacher, P. W. M. Peters and B. Skrotzki: Materials Science and Engineering A 452-453(2007) pp. 536-544.
6) R. Leucht and H. J. Dudek: Materials Science and Engineering A 188(1994) pp. 201-210.
7) S. M. Jeng and J. M. Yang: Materials Science and Engineering A 171(1993) pp. 65-75
8) C. leyens, J. Hausmann and J. Kumpfert: Advanced Engineering Materials 5(2003) pp. 399-410.
9) C.Badini, G. Ubertalli, D. Puppo and P. Fino: Journal of Materials Science 35(2000) pp. 3903-3912.
10) M. Hagiwara, N. Arimoto, S. Emura, Y. Kawabe and H. G. Suzuki: ISIJ International 32(1992) No.8 pp. 909-916.
11) S. C. Tjong and Yiu-Wing Mai: Composites Science and Technology 68(2008) pp. 583-601.
12) W. O. Soboyejo, R. J. Lederich and S. M. L. Sastry: Acta Metall 42(1994) pp. 2579-2591.
13) S. Gorsse and D. B. Miracle: Acta Materialia 51(2003) pp. 2427-2442.
14) T. Threrujirapapong, K. Kondoh, H. Imai, J. Umeda and B. Fugetsu: Materials Transactions 50(2009) No.12 pp. 2757-2762.
15) A. Ma, J. Jiang, N. Saito, I. Shigematsu, Y. Yuan, D. Yang and Y. Nishida: Materials Science and Engineering. A513-514(2009) pp. 122-127.
16) B. Martin, S. Frantisek, B. Otto and G. Requena: Materials Science and Engineering. A504(2009) pp. 1-7.
17) A. P. Zhilyaev, K. Ohishi, T. G. Langdon and T. R. McNelley: Materials Science and Engineering. A410-411(2005) pp. 277-280.
18) A. V. Sergueeva, V. V. Strolyarov, R. Z. Valiev and A. K. Mukherjee: Scripta Materialia. 45(2001) pp. 747-752.
19) T. Yoshimura, H. Imai, T. Threrujirapapong and k. Kondoh: Materials Transactions 50(2009) No. 12 pp. 2751-2756.
20) E. O. Hall: Proc. Phys. Soc. 64B(1951) 747.
21) N. J. Petch: J.Iron Steel Inst. 173(1953) 25.
22) Y. Kobayashi, Y. Tanaka and K. Matsuoka: J.Soc. Mat. Sci.,Japan. 54(2005) pp. 66-72.