High performance Ti-6Al-4V alloy by creation of harmonic structure design

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Abstract: Ti-6Al-4V alloy is an advanced structural material having applications in a wide range of areas spanning from biomedical to aerospace sectors due to the excellent combination of mechanical and chemical properties. In the present work, a new tailored heterogeneous microstructural design with a specific topological distribution of fine and coarse grained areas, called “harmonic structure”, has been proposed for the strengthening of Ti-6Al-4V alloy to achieve improved performance of the components in service. It has been demonstrated that Ti-6Al-4V alloy with harmonic structure can be successfully prepared via a powder metallurgy route consisting of controlled severe plastic deformation of pre-alloyed powders via mechanical milling followed by their consolidation. The Ti-6Al-4V compacts with harmonic structure design exhibited significantly better strength and ductility, under quasi-static as well as rapid loading conditions, as compared to their homogeneous fine and coarse grained counterparts. It was found that the harmonic structure design has the ability to promote the uniform distribution of strain during plastic deformation, leading to improved mechanical properties by avoiding localized plastic instability.

1. Introduction

Ti-6Al-4V alloy is widely used for a variety of structural applications, including bio-implants and airframes, owing to its exceptional combination of mechanical and chemical properties [1-3]. However, comprehensive research efforts are being made for improving mechanical properties to improve reliability in performance. The improved properties would also prove effective in cost reduction by providing high strength small sized components and avoiding the frequent replacements of the components. The microstructural refinement is a very attractive and efficient way of strengthening
metals and alloys. In recent years, efforts have been made to improve the mechanical properties of Ti-6Al-4V alloy via grain refinement wherein the ultra-fine grained (UFG) Ti-6Al-4V alloys exhibited significantly higher yield and fracture strengths as compared to the coarse-grained (CG) Ti-6Al-4V alloys with similar compositions [4-12]. However, the grain refinement led to inferior ductility in UFG Ti-6Al-4V alloys as compared to their CG counterparts, as observed in case of most of the other materials with UFG microstructure. Therefore, it would be worth making efforts towards development of Ti-6Al-4V alloys with high strength and high ductility to meet the demand for stronger and tougher Ti-6Al-4V alloy for improved and reliable performance in service.

Recent research efforts have shown that the metals and alloys with bimodal grain size distribution are very effective in achieving an attractive combination of reasonable ductility and high strength [13-17]. In particular, Ameyama and co-workers proposed an exquisite microstructural design, called “harmonic structure”, which essentially a bimodal microstructure wherein the coarse-grained areas (“core”) are present as embedded islands in the matrix of three-dimensional continuously connected network (“shell”) of fine-grained areas [17-22]. Bulk SUS329J1 steel [20], Co-Cr-Mo alloy [21] and SUS304L steel [22] with harmonic structure design were successfully prepared. The harmonic structured materials demonstrated significantly better combination of strength and ductility as compared to their homogeneous fine or coarse-grained counterparts. It is envisaged that the harmonic structure Ti-6Al-4V alloys would also exhibit an attractive combination of mechanical properties, such as high strength together with high ductility.

Therefore, the present work deals with the preparation and evaluation of harmonic structure Ti-6Al-4V alloy. The Ti-6Al-4V alloy with harmonic structure design was prepared by powder metallurgy route involving controlled mechanical milling of the pre-alloyed powders and spark plasma sintering. The microstructural characteristics of the initial pre-alloyed, milled, and sintered powders are presented and discussed. The mechanical properties and deformation behaviour of the harmonic structured Ti-6Al-4V alloy were also studied, and are compared with those of the homogeneous coarse grained acicular microstructure. Finally, an attempt has been made to understand the deformation mechanism which leads to a combination of high strength and high ductility in materials with harmonic structure design.

2. Experimental Procedure
In this work, the starting material was pre-alloyed Ti-6Al-4V alloy powder prepared from plasma rotating electrode process (PREP) and having average particle size of approximately 186 µm. The Ti-6Al-4V alloy powder had following composition (mass %): Fe=0.183, O=0.198, C=0.010, N=0.010, H=0.0008, Al=6.55, V=4.26, Ti= balance. The powder was mechanically milled (MM) in a planetary
ball mill (Fritsch P-5) using vials, filled with argon gas, and steel balls. The milling was carried out at a rotation speed of 200 rpm for 90 ks (25h) having ball-to-powder ratio 1.8. Subsequently, both the initial and MMmed PREP powders were consolidated by spark plasma sintering (SPS,) using a graphite die with 15 mm internal diameter, at 1123 K (850 °C) for 1.8 ks (30 minutes) under vacuum and 50 MPa applied pressure. The heating and cooling rate during sintering were approximately 65 and 225 K/min, respectively.

The microstructural characteristics of the initial powder, MMed powder, and the sintered compacts were observed by scanning electron microscope (SEM), electron backscattered diffraction (EBSD) technique, and transmission electron microscope. The specimen for TEM observations were made by focused ion beam (FIB) method. The mechanical properties of the materials were evaluated by hardness measurements and tension tests. An average of 25 measurements was considered as the representative average hardness of the material. The tensile tests were carried out on specimens having gauge dimensions 3 mm (length) x 1 mm (width) x 1 mm (thickness), using a Shimadzu AGS-10kND tensile testing machine at a strain rate of 5.6x10^{-4} s^{-1}.

3. Results and Discussion

3.1. Microstructure of the Initial and Milled Ti-6Al-4V Alloy Powders

Figure 1 shows the morphology and cross-section of the initial and MM PREP powders. The initial PREP powders were spherical in shape with almost smooth surface (Figure 1a) and acicular microstructure (Figure 1b). The powder particles attained spherical shape due to surface tension to minimize surface area during PREP. The acicular microstructure is a typical feature of rapidly cooled Ti-6Al-4V alloys due to the presence of $\alpha'$ martensite [2]. On the other hand, the morphology (Figure 1c) and the microstructure of the cross-section of the milled powders (Figure 1d) shows that the controlled milling led to the formation of featureless region, having “shell-like” appearance, in the vicinity of the surface of the powder particles whereas the remaining inner part of the milled powder particles, i.e. “core” of the powder, still consisted of acicular microstructure. The micro-hardness measurements on the initial and milled PREP powders, as depicted on the Figure 2b and 2d, show that the hardness of the “shell” region is significantly higher than that of the “core” region, indicating that the milling-induced severe plastic deformation was limited primarily to the near-surface regions of the powder particles in the form of severely deformed featureless “shell” region.

Figure 2 shows a TEM micrograph, and its corresponding SAD pattern, of the milled powder depicting the microstructure of the severely deformed featureless “shell” region. The TEM micrograph, together with “ring-type” SAD pattern, clearly shows that the sub-surface region in the immediate vicinity of the powder surface consisted of almost equiaxed nano-sized grains/crystallites followed by presence of deformed elongated grains in the areas slightly away from the surface. The above results,
along with the presence of significant amounts of dislocations, indicate that the milling-induced severe plastic deformation led to grain refinement via fragmentation and subdivision of the initial coarse grains. Hence, the controlled mechanical milling resulted in the formation of a bimodal microstructure in the milled powder particles, i.e. (i) nanocrystalline “shell” region in the vicinity of the surface of the particle, and (ii) moderately deformed coarse-grained “core” inner region.

**Figure 1:** Morphology and Cross-section of the (a & b) Initial PREP, and (c & d) MM powders
Figure 2: A typical TEM micrograph, and its corresponding SAD pattern, depicting the area near the surface of the MMed PREP Ti-6Al-4V powder

3.2. Microstructure of the Sintered Ti-6Al-4V Compacts

Figure 3 shows the microstructures of the Ti-6Al-4V alloy specimens prepared from conventionally cast alloys and milled PREP powders. The specimens prepared from the conventionally cast alloy exhibit coarse acicular microstructure (Figure 3a). The coarse acicular/lath type microstructure is a typical characteristic associated with the formation of α+β microstructure in the Ti-6Al-4V alloys [1-3]. On the other hand, the milled bimodal PREP powders resulted in equiaxed as well as coarse acicular/lath type structure with a peculiar topological distribution wherein the regions with acicular/lath type structure are embedded in the matrix of fine-equiaxed grains. Such a peculiar bimodal microstructure, i.e. regions with fine-equiaxed grains form a continuous connected three dimensional network around the regions with coarse acicular/lath type microstructure, is referred as “Harmonic” structure design wherein the regions with equiaxed and acicular morphology correspond to the severely deformed “shell” and un-deformed “core” regions of the milled powders, respectively. Interestingly, Figure 3b also indicates that the shell region appears to have regions with different grain sizes, i.e. relatively finer grain size in the middle region as compared to the outer region of the shell area.
The formation of fine-grained equiaxed structure after sintering at sufficiently elevated temperatures and the difference in the grain size in the shell region are interesting and peculiar features. These microstructural features appears to be related with the gradient of degree of plastic deformation in the MMed powder, from the surface towards the center of the milled powder, and other factors affecting the nucleation and growth of the strain free grains. The equiaxed nano-sized grains in the immediate vicinity of the deformed particle surface can be considered as large number of strain-free nuclei. It appears that, during sintering, these nuclei grow together followed by the impingement of the high angle grain boundaries. The formation of relatively larger equiaxed grains in the outer-shell region appears to be governed by the recovery and recrystallization process in the plastically deformed region with elongated grains and high dislocation density. However, the role of interstitial elements, such as oxygen, nitrogen, and carbon atoms, together with titanium oxide particle and β phase precipitates in the Ti-6Al-4V alloy on the excellent thermal stability of the fine-grained structure cannot be ruled out [11].

3.3. Mechanical Properties and Deformation Behavior

Figure 4 shows the representative nominal stress – nominal strain curves of the Ti-6Al-4V alloy specimens with conventional-acicular as well as harmonic structure. The average values of yield strength, tensile strength, and fracture strain are also provided in Table 1. It can be clearly observed that the sintered compacts with harmonic structure exhibited considerably higher yield strength, tensile strength, total strain-to-fracture, and uniform elongation as compared to those of the specimens with coarse grained acicular microstructure. Moreover, these results also indicated that the harmonic structured Ti-6Al-4V exhibit superior set of mechanical properties as compared to their ultra-fine grained counterparts [5-12]. Therefore, the harmonic structure design proved extremely effective in
achieving higher strength without compromising ductility in the Ti-6Al-4V alloys, i.e. improved toughness as compared to the conventional homogeneous microstructures.

![Nominal Stress-Strain curves](image1.png)

**Figure 4:** Nominal Stress-Strain curves of Ti-6Al-4V specimens with conventional acicular and harmonic microstructures

![True Stress-Strain and SHR curves](image2.png)

**Figure 5:** True Stress-Strain and SHR curves of acicular and harmonic Ti-6Al-4V specimens

| Property               | Homo-Acicular | Harmonic |
|------------------------|---------------|----------|
| Yield Stress (MPa)     | 835           | 950      |
| Uniform Elongation (%) | 5.9           | 6.4      |
| Tensile Strength (MPa) | 934           | 1043     |
| Total Strain-to-fracture (%) | 18.7       | 22.7    |

**Table 1: Mechanical properties of conventional acicular and harmonic structure Ti-6Al-4V alloy**

Figure 5 shows the true stress – true strain curves, along with their corresponding strain hardening rate (SHR) curves, of the Ti-6Al-4V compacts with harmonic as well as acicular coarse grained microstructure. It can be observed that the harmonic structured specimens exhibited relatively smaller strain hardening rate in the early stages of deformation as compared to the coarse grained acicular structure, followed by comparable strain hardening rates. Then after, the SHR of harmonic structure remains slightly higher during subsequent deformations. The lower SHR in the early stages of deformation is a typical characteristic of the relatively fine-grained materials. Therefore, the
deformation behavior of the harmonic structure can be divided in two stages: (i) early stages of
deformation similar to homogeneous fine-grained microstructure as characterized by lower SHR, and
(ii) large uniform deformation and higher SHR in the later stages typical to coarse grained materials.

In order to further understand the difference between the deformation mechanism of harmonic and
homogeneous acicular microstructures, reduction in the thickness of the gauge section of the tensile
test specimens were made. Figure 6 shows the relative reduction in thickness of the gauge section at
various locations after approximately 4% deformation. It can be seen that the acicular microstructure
exhibits extremely localized strain accumulation whereas the harmonic structure exhibits relatively
uniform distribution of strain after significant plastic deformations. These results indicate that the
harmonic structure promotes uniform distribution of strain during plastic deformation. It would be
worth mentioning that, recently, Dirras and co-workers have observed that the harmonic structure
promotes uniform distribution of strain under rapid deformation conditions also.

Figure 7 depicts the deformation mechanism of harmonic structured Ti-6Al-4V alloy based
on the above discussion. It appears that the early stage of deformation is dominated by the deformation
of the strong fine-grained shell. As soon as the material is deformed, the stronger “shell” undergoes
shape change to accommodate the shape change of the specimen. During this process, the relatively
soft “core” also undergoes plastic deformation to accommodate the shape change of the “shell” to
maintain the structural integrity of the material, leading to the strain hardening and increased strength
with increasing straining. The subsequent straining leads to further accumulation of strain in the
“core” and strain hardening, until the strength of the “core” reaches a value comparable to the
fine-grained “shell”. Thereafter, the whole structure deforms as a homogeneous material until fracture.
Hence, the higher strength in the harmonic structure is derived from the stronger “shell” whereas the
high ductility is achieved from the accommodation of plastic deformation by the soft “core” regions.

Furthermore, the harmonic structure also promotes uniform distribution of strain during plastic
deformation owing to the peculiar topological distribution of strong and ductile regions. As a result, a
combination of high strength and high ductility is achieved in the harmonic structured materials.
4. Conclusions

The harmonic structure was successfully created by controlled mechanical milling of the pre-alloyed Ti-6Al-4V powder followed by spark plasma sintering. The controlled mechanical milling resulted in
the powder particles with bimodal grain size distribution consisting of severely deformed nanocrystalline “shell” region in the vicinity of the surface of the particle and coarse-grained “core” inner region. Spark plasma sintering of milled powder leads to the formation of “harmonic” structure wherein the severely deformed shell regions of the milled powders form a three dimensional network of equiaxed ultrafine-grains, enclosing the coarse-grained “core” areas. The harmonic Ti-6Al-4V alloys exhibited a significant enhancement in the strength without compromising with the ductility, i.e. improved toughness as compared to the conventional homogeneous coarse/fine-grained microstructures. The improved mechanical properties of the harmonic Ti-6Al-4V were attributed to the peculiar topological distribution of strong fine-grained “shell” and ductile coarse-grained “core” regions, which promotes uniform distribution of strain during plastic deformation, leading to improved mechanical properties by avoiding the localized plastic deformation in the early stages of deformation.

5. References
[1] Boyer R 1996 Mater. Sci. Eng. A 213 103.
[2] Leyens C and Peters M 2003 Titanium and Titanium Alloys (WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim) 1-496.
[3] Boyer R, Welsch G and Collings EW 1994 Materials Properties Handbook – Titanium Alloys (ASM International, OH ) 483-636.
[4] Sergueeva AV, Stolyarov VV, Valiev RZ and Mukherjee AK 2000 Scripta Mater. 43 819.
[5] Mishra RS, Stolyarov VV, Echer C, Valiev RZ and Mukherjee AK 2001 Mater. Sci. Eng. A 298 44.
[6] Salishchev GA, Galeyev RM, Valiakhmetov OR, Safiullin RV, Lutfullin RY, Senkov ON, Froes FH and Kaibyshev OA 2001 J. Mater. Proc. Tech. 116 265.
[7] Sergueeva AV, Stolyarov VV, Valiev RZ and Mukherjee AK 2002 Mater. Sci. Eng. A 323 318.
[8] Zhurebtsov SV, Salishchev GA, Galeyev RM, Valiakhmetov OR, Mironov SY and Semiatin SL 2004 Scipta Mater. 51 1147.
[9] Ko YG, Lee CS, Shin DH and Semiatin S 2006 Metall. Mater. Trans. A 37A 381.
[10] Zhurebtsov S, Kudryavtsev E, Kostjuchenko S, Malyshova S and Salishchev G 2012 Mater. Sci. Eng. A 536 190.
[11] Long Y, Zhang H, Wang T, Huang X, Li Y, Wu J and Chen H 2013 Mater. Sci. Eng. A 585 408.
[12] Murty SV, Nayan N, Kumar P, Narayanan PR, Sharma SC and George KM 2014 Mater. Sci. Eng. A 589 174.
[13] Wang Y, Chen M, Zhou F and Ma E 2002 Nature 419 912.
[14] Witkin D, Lee Z, Rodriguez R, Nutt S and Lavernia E 2003 Scripta Mater. 49 297.
[15] Wang YM and Ma E 2004 Acta Mater. 52 1699.
[16] Dirras G, Gubicza J, Ramtani S, Bui QH and Szilagyi T 2010 Mater. Sci. Eng. A 527 1206.
[17] Fujiwara H, Akada R, Noro A, Yoshita Y and Ameyama K 2008 Mater. Trans. 49 90.
[18] Sekiguchi T, Ono K, Fujiwara H and Ameyama K 2010 Mater. Trans. 51 39.
[19] Orlov D, Fujiwara H and Ameyama K 2013 Mater. Trans. 54 1549.
[20] Ciuca OP, Ota M, Deng S and Ameyama K 2013 Mater. Trans. 54 1629.
[21] Sawangrat C, Yamaguchi O, Vajpai SK and Ameyama K 2014 Mater. Trans. 55 99.
[22] Zhang Z, Vajpai SK, Orlov D and Ameyama K 2014 Mater. Sci. Eng. A 598 106.
[23] Munir ZA, Tamburini UA and Ohyanagi M 2006 J. Mater. Sci. 41 763.

Acknowledgements

This research was supported by the Japan Science and Technology Agency (JST) under Collaborative Research Based on Industrial Demand “Heterogeneous Structure Control: Towards Innovative Development of Metallic Structural Materials”, and by the Grant-in-Aid for Scientific Research on Innovative Area, “Bulk Nanostructured Metals”, through MEXT, Japan (contract No. 22102004). These supports are gratefully appreciated.