New Microstructure Design for Commercially Pure Titanium with Outstanding Mechanical Properties by Mechanical Milling and Hot Roll Sintering

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Commercially pure titanium powder is subjected to mechanical milling (MM)—a severe plastic deformation process—for various periods of time. The MM powder has two different kinds of microstructure, which can be controlled by the MM conditions. They include ultrafine and coarse grain structures known as “shell” and “core”, respectively. Subsequently, these MM powder is sintered using a hot roll sintering (HRS) process. The HRS materials with the shell and the core have a network structure of continuously connected shells, which is known as a harmonic structure. The HRS materials with the harmonic structure simultaneously demonstrate both high strength and elongation. These outstanding mechanical properties are influenced by the harmonic structure characteristics such as shell and core grain sizes, and shell fraction and shell network size. Thus, the harmonic structure can be considered as a remarkable design for improving the mechanical properties of commercially pure titanium as well as other metallic materials. [doi:10.2320/matertrans.MB200913]

(Received August 18, 2009; Accepted November 4, 2009; Published December 16, 2009)

Keywords: metallic powder, severe plastic deformation, harmonic structure, titanium, mechanical property, microstructure

1. Introduction

Titanium is a promising material because of properties such as a high strength-density ratio and its high corrosion resistance. Particularly, commercially pure titanium will be applied to medical products because it has both good corrosion resistance and biocompatibility. In this regard, many researchers have focused on its microstructure design, and mechanical properties, physical and chemical properties. It is well known that those properties, especially the mechanical properties, are very sensitive to microstructural factors such as grain size; hence the grain refinement of the metallic materials is one of the beneficial method for improving mechanical properties. Recently, the severe plastic deformation (SPD) process¹,² has received much attention since it efficiently fulfills the grain refinement of the metallic materials. High pressure torsion (HPT),³ equal channeling angular pressing (ECAP)⁴,⁵ and accumulative roll bonding (ARB)⁶ are such bulk-SPD processes. Mechanical milling (MM) and alloying (MA)⁷–¹⁶ are SPD-powder metallurgy (PM) processes. Most of those bulk-SPD processes have an advantage that the materials retain almost the same shape after processing, whereas the SPD-PM process can be easily transferred to the conventional PM process, which has been applied for hundreds of years. However, the metallic materials with homogeneous ultra-fine grain structure pose a serious problem; the ultra-fine grain materials indicate quite high strength but have limited ductility due to their plastic instability.¹⁷

In the present study, we propose a new microstructure design for the commercially pure titanium powder. This new microstructure design could solve the problem by homogeneous ultra-fine grained materials as described above. It is a high possibility that the mechanical milling process combined with a hot roll sintering (HRS) process for metallic powder makes a bimodal microstructure (harmonic structure). Further, it has been reported that the metallic materials with harmonic structure indicate superior mechanical properties.¹⁴–¹⁶ The relationship between the microstructure and mechanical properties of commercially pure titanium powder subjected to the MM and HRS are discussed in detail.

2. Experimental Procedures

Commercially pure (CP) titanium powder was provided for the experiments and its chemical composition is shown in Table 1. The CP titanium powder with particle sizes ranging from approximately 100 to 180 μm was produced using the plasma rotating electrode process (PREP).¹⁸ The powder fabricated by the PREP process was spherical and are insignificantly contaminated by impurities such as oxygen or nitrogen gases during the fabrication process.¹⁸ The MM powder was performed on a Fritch P-5 planetary ball mill with tungsten carbide vial and SUS316 stainless steel balls in the argon gas atmosphere at room temperature. In order to avoid contamination caused by the milling media, conventional CP titanium powder with average particle size of 45 μm was milled for 86.4 ks to make a titanium-coating-layer on the surface of both vial and balls.¹⁹ Furthermore, no process agent was used during the milling. The milling intensity can be controlled by selecting the ball-to-powder weight ratio and process time. Their values chosen were 1.8 : 1 and from 3.6 to 1080 ks, respectively. The MM powder was sintered

| Table 1 Chemical composition of as-received commercially pure (CP) titanium powder. (mass%) |
|---|---|---|---|---|---|---|---|
| Fe | O | C | N | H | Ti |
| 0.04 | 0.111 | 0.004 | 0.015 | 0.012 | bal. |

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using a HRS process. A CP titanium pipe filled with MM powder was evacuated and sealed. Then hot rolling was carried out five times at 1173 K to produce a 1.2 mm sheet by 90% reduction. Subsequently, the initial titanium pipe portion was removed from the HRS material by grinding. The oxygen content of the HRS materials was analyzed by means of the inert gas fusion–infrared absorption method (on a LECO TC436AR). Table 2 lists the oxygen contents of the HRS materials fabricated from three kinds of the powders, i.e., without-milling (MM0s), milled for 3.6 ks (MM3.6ks) and milled for 90 ks (MM90ks). Because of the above-mentioned titanium pre-coating treatment, neither the MM treatment nor the HRS process raise the oxygen content of the powders or the compacts so much. The microstructure of the HRS materials was characterized by means of scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Thin foils for TEM observation were prepared by using a focused ion-beam (FIB). The Kroll solution was used as etchant for the specimens for SEM observation.

The mechanical properties were examined using hardness and tensile tests. The micro-Vickers hardness was tested at a load of 0.245 N. The measurement was carried out at one hundred random points in each specimen. The tensile test was carried out using a Shimadzu AGS-10kND tensile testing machine at an initial strain rate of $8.5 \times 10^{-4} \text{s}^{-1}$. Tensile tests were performed on specimens with 10 mm in gauge length, 2 mm in width, and 1 mm in thickness.

3. Results and Discussion

3.1 Microstructure of MM powder

Figure 1 shows SEM micrographs of the CP titanium powder before and after milling for time periods of 3.6 to 180 ks. The initial powder shows a spherical and a smooth appearance, whereas the MM powder shows an irregular shape. Although the powder appearance became more irregular with increased milling time, none of the powder milled up to 180 ks exhibited any agglomerates, and the powder particle size was maintained.

Figure 2 shows cross-sectional SEM micrographs of a powder mechanically milled for 90 ks (hereafter, referred to as “MM90ks powder”). Figure 2(b) shows an enlarged image of the selected rectangular area indicated in Fig. 2(a). As can be seen in Fig. 1(a) and (b), the powder microstructure is able to be classified by the outer and inner regions. Hereafter, these outer and inner regions are referred to as “shell” and “core”, respectively. Because the shell has deformed heavier than the core, the difference of the contrast in the powder was observed. The average hardnesses of the shell, core and initial CP titanium powder were Hv 281, Hv 264 and Hv 183, respectively.

Figure 3 shows TEM micrographs in the vicinity of the shell region of the MM90ks powder. Figure 3(b) and (c) are
enlarged images, which correspond to the selected rectangular areas indicated as A and B in Fig. 3(a). In Fig. 3(b), close to the surface region, equiaxed grains with less than 100 nm in diameter are observed. As indicated in Fig. 3(c), a nano layer structure with elongated grains is observed in deeper regions of the powder. The present authors have previously reported that the formatting of equiaxed nano grain structure in MM powder occurs because of the grain sub-division and rotation of those elongated grains. 12–14,19–22) Not only titanium, but also copper, 20) iron, 20) nickel, 21) tungsten, 19,22) and austenitic stainless steel 12–14,19,21) powder demonstrate almost the same equiaxed nano grain structure after the mechanical milling process. Formation of the nano grains depends on the stacking fault energy since dislocation accumulation by milling is extremely important for the grain sub-division. 23–26)

3.2 Microstructure of the HRS materials

Figure 4 shows SEM micrographs of the HRS sheet, which is fabricated with MM90ks powder, taken from the rolling, the normal and the transverse directions (RD, ND and TD). An elongated pancake grain structure that is perpendicular to the ND can be observed in the SEM micrographs at the RD and TD. Few pores were observed except at the edge of the sheet; therefore, the HRS process is efficient for fabricating a high density powder compact.

Figure 5 shows an SEM micrograph of the HRS material at the ND fabricated with MM90ks powder and its schematic illustration. The HRS material indicates two different microstructures: a dark and smooth region, and a bright and rough region. The smooth and rough regions correspond to the shell and the core in the MM powder. The shell region forms a
network structure and the core region is surrounded by the shell network. Hereafter, such a network structure of shell and core is referred to as a “harmonic structure”.

Figure 6 shows a TEM image of the shell in the harmonic structure, which is formed in the HRS material fabricated with MM90ks powder. An ultra-fine grain structure with grain size ranging from 300 to 500 nm in diameter is observed. On the other hand, the core region consists of coarse grains of several microns in diameter.

From the microstructure observations as shown in Figs. 1 to 6, the shell and core structure in the MM powder and the harmonic structure in HRS material can be summarized in Fig. 7. Figure 7 shows illustrations of the MM powder and the HRS material, respectively. In the MM powder, the shell

Fig. 6  TEM micrograph of shell area in HRS material (MM90ks).

Fig. 7  Schematic illustrations of (a) milled powder and (b) HRS material. (a): mechanically milled powder has “shell” and the “core”. (b): HRS material has “harmonic structure”.

Fig. 5  Cross sectional SEM micrograph of (a) HRS material MM90ks. (b) is schematic illustration.
has a fine grain structure, while the core has a coarse grain structure. When the MM powder is sintered by hot rolling, bonding of every shell region occurs in the same manner as conventional sintering of the PM; this leads to the formation of a strong network structure. The most significant difference between the harmonic structure and the conventional composite material structure is that all the shells in the harmonic structure are interconnected in the continuous network. Therefore, the harmonic structure is expected to have unique mechanical properties.

3.3 Mechanical properties of the HRS materials

Figure 8 shows the distribution of micro-Vickers hardness of HRS materials fabricated for various MM time. The results of the MM0s, MM3.6ks and MM18ks HRS materials show a single hardness peak, which shifts to greater values with increasing MM time. However, in the results from the MM36ks to MM180ks powder, the hardness profile spreads and two peaks are observed. When the milling time exceeds 360 ks, the profile becomes narrower and the double peak disappears. It is interesting that the constant hardness value or the double hardness peaks of the HRS materials appear under the same milling condition. This is caused by the difference between the hardness of the shell and core regions. The unique phenomena of change in hardness of the MM powder and the HRS materials can be understood by the microstructural changes; that is, both the shell and the core structures appear in the MM powder for the certain period of MM time because the shell is generated at the very edge of the powder surface and grows during milling. The volume fraction of the shell increases with MM time, and the shell finally occupies a large portion of the powder and thus the second hardness peak disappears. Moreover, it is important that the specific characteristics of the MM powder can be retained even after the HRS process.

Nominal stress–nominal strain curves of the HRS materials obtained from tensile tests are shown in Fig. 9. In this figure, (a) and (d) are the results of the 90% cold rolled (C.R.) and as-received bulk material, respectively, while (b) and (c) are the results of HRS materials of MM90ks powder and MM0s powder, respectively. The HRS material, fabricated with an MM90ks powder demonstrates relatively high strength and elongation as compared to those of the CP titanium bulk material. Figure 10 indicates the relationship between ultimate tensile strength (UTS) and total elongation of HRS materials (MM 0 to 90 ks) and 90% C.R., Bulk and 90% hot rolled at 1173 K (H.R.).
Figure 11 indicates the relationships of UTS, total elongation, and shell and core grain sizes. The shell and core grain sizes correspond to the average grain sizes in the shell and core area, respectively. It is clear that the UTS and the shell grain size are inversely proportional, whereas total elongation and the core grain size are directly proportional. However, no effect of shell grain size on elongation and no effect of the core grain size on UTS are observed. In the case of the SUS316L HRS materials, the shell volume fraction is the quite significant factor for the UTS, and both the proof stress and UTS increased with the volume fraction of shell. In the present study, the shell fractions in all of the HRS materials were approximately 45%. These results imply that the shell grain refinement could improve the strength as well as the increment of shell fraction. However, when the shell fraction exceeds more than 50%, the elongation of SUS316L HRS materials tend to decrease. Therefore, the shell and core in the harmonic structure significantly influences both the strength and ductility. Moreover, as shown in Figs. 9 and 10, the UTS and elongation of the CP titanium with a harmonic structure were approximately 750 MPa and 20%, respectively, which are superior results to those of conventional austenitic stainless steels such as SUS316L. These results show that the CP titanium with a harmonic structure can replace SUS316L for biomaterial applications.

4. Conclusions

Commercially pure (CP) titanium powder fabricated using a plasma rotation electrode process was mechanically milled and sintered by a hot roll sintering (HRS) process, which is one of the severe plastic deformation powder metallurgy processes. The conclusions are obtained as follows:

1. By controlling the mechanical milling conditions, two different kinds of microstructures are generated. An ultra-fine grain structure formed in the near surface region (shell), and a coarse grain structure remains in the inside of the powder (core).
2. HRS materials of powder milled for 36 to 180 ks show two hardness peaks, that is, the shell has higher hardness than that of the core.
3. HRS materials with a harmonic structure have a network structure composed of continuously connected shell and dispersed core regions.
4. HRS materials with a harmonic structure demonstrated outstanding mechanical properties such as high strength and elongation. Therefore, having harmonic structure is able to improve the strength and ductility at the same time.
5. The tensile strength of HRS materials can be raised by the shell grain refinement, while the elongation can be increased with an increase of the core grain size. Therefore, by changing the shell and core grain sizes, shell fraction and shell network size, the mechanical properties of metallic materials with a harmonic structure could be controlled.

Acknowledgements

Part of this study was supported by a Grant-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan on Priority Areas “Giant Straining Process for Advanced Materials Containing Ultra-High Density Lattice Defects”.

![Fig. 11 Relationships between UTS, total elongation and (a) shell grain size or (b) core grain size.](image-url)
REFERENCES