Effect of Zirconia Addition on Strengthening Ability of Titanium Alloys Prepared by Powder Metallurgy

N. Vorapattanapaibul, K. Kondoh and A. Khantachawana

Abstract— Ti6Al4V alloy has been widely used in medical applications because of its outstanding mechanical properties and formability. However, it is reported that Aluminum (Al) and Vanadium (V) can cause Alzheimer’s disease and cytotoxicity. Then, present researches pay much more interest in non-toxic Ti alloys without losing the strength. The present study aims to investigate the strengthening effect of ZrO_2 addition into Ti powder fabricated by Spark Plasma Sintering (SPS) method. Titanium (Ti) powder and ceramic compound, Zirconia (ZrO_2) powder were mixed together and consolidated by SPS followed by heat treatment and hot extrusion, respectively. It is confirmed that, 1 wt% of ZrO_2 was completely decomposed after spark plasma sintering and solid solution inside Titanium matrixes without changing grain size. It is clear that both hardness and tensile strength were significantly increased by solid solution hardening with adding 1wt% of ZrO_2 compared with pure Titanium.

Keywords—Titanium, Zirconia, Powder Metallurgy, Spark Plasma Sintering.

I. Introduction

Titanium (Ti) and its alloy are widely used in several applications such as aerospace, automotive, biomedical, etc. [1]-[4] due to their excellence in mechanical properties, corrosion resistance and biocompatibility [5]. One of the most widely used materials in biomedical field is Ti-6Al-4V alloy [1]. However, there are some reports mentioned that Vanadium (V) is cytotoxicity and Aluminum (Al) is risk to cause an Alzheimer’s disease [6], [7]. Hence, there is a challenge for researchers to find alternative alloying elements that has good corrosion resistance and biocompatibility whereas mechanical properties remain compatible with bulk Titanium alloys. To attain those requirements, Zirconium Dioxide (ZrO_2) is an attractive alloying material. According to the periodic table, Zirconium (Zr) is biocompatible and has relatively similar chemical properties and crystal structure with those of Titanium [8]. Moreover, Ti-Zr phase diagram shows that Zr can be dissolved into Ti matrix without a limit, on the other word, solid solution hardening can be expected [9]. Besides, Ti-O phase diagram also shows that Oxygen is at 34 at% able to be dissolved in α-Titanium [10]. Thus, favorable mechanical properties of this Al-V-free Titanium alloys might could be expected from the solid solution strengthening. However, ZrO_2 is a ceramic compound with high melting temperature, resulting in high energy consumption-during melting process [11]. Powder metallurgy could enhance this limitation since it consolidates the sample in solid-state which consume lower energy. Moreover, it has other practical consolidation advantages such as near-net shape, etc. [12].

In the present study, Ti+ZrO_2 powder alloys were prepared by spark plasma sintering method. Mechanical behavior and microstructure were investigated in order to evaluate strengthening ability of ZrO_2 addition.

II. Methods

Titanium (Ti) powder (purity 99.4%, 45 μm) and ZrO_2 powder (purity 98%, 1 μm) were prepared. Ti+1wt%ZrO_2 alloy was fabricated by mixing the materials together with 0.02wt% lubricant oil followed by rocking milled at 60 Hz for 1 hour. Pure Ti was also fabricated for comparison. Summarization of the designed alloy compositions are shown in Table I.

TABLE I: Compositions of Ti+ZrO_2

Condition	Composition
Ti+0ZrO_2	100 wt% Ti
Ti+1ZrO_2	100 wt% Ti + 1 wt% ZrO_2

Prepared powder was then consolidated into billet shape with diameter of 42 mm by using spark plasma sintering machine (DR.SINTER) at temperature of 1100℃ for 3 hours under compressive pressure at 30 MPa in vacuum atmosphere, then furnace cooled. Homogenization was carried out by heat treatment at 1000℃ for 3 hours in vacuum atmosphere followed by furnace cooling. Hot extrusions were performed by pre-heating the die to 400℃ and the billet was pre-heated to temperature 850℃ for 10 mins under Argon gas atmosphere with flow rate of 5 L/min. The die and billet were then rapidly removed from furnace to the hot pressing machine and perform hot extrusion under pressure of 600 MPa with ram speed of 6 mm/s at extrusion ratio of 18.5. The final specimens were obtained in rod shape diameter and length of 10 mm and 15 cm

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respectively.

X-Ray Diffraction (XRD) tests were performed in SHIMADZU LabX XRD-6100 using CuKα radiation, with the scanning rate of 0.2°/min. Microstructures were observed by optical microscope OLYMPUS DSX 500. Vickers micro hardness tests were performed by hardness tester machine SHIMADZU HMV with test load of HV0.5 and holding time of 15s. Relative density were measured by Archimedes method in ALFA MIRAGE Electronic densimeter MDS-300. Oxygen and Nitrogen content were evaluated by HORIBA EMGA-830 OK Oxygen Nitrogen Hydrogen Analyzer. The rods were then milled into the shape as shown in Fig. 1 (unit: millimeter) with the gauge length of 9 mm. Universal tensile tests were performed in SHIMADZU Autograph AG-X 50 kN load cell with the strain rate at 5.0 x 10^{-4} /s.

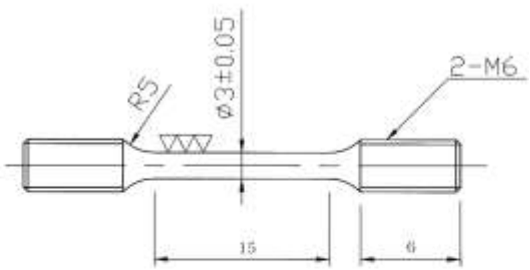

Fig. 1 Sketch of the tensile sample

III. Results & Discussions

Fig. 2 and Fig.3 shows the XRD profiles of each specimen in each process obtained from Ti+0ZrO_2 and Ti+1ZrO_2 alloy, respectively. For the specimen without ZrO_2, main peaks of α-Titanium are common to be observed. It is noted that a peak at diffraction angle around 25° is possibly came from the mounting resin. According to Fig. 3, the peaks of α-ZrO_2 powder before mixing were clearly observed. However, after mixing with Titanium powder, the intensity of α-ZrO_2 significantly decreases due to little amount of addition ZrO_2 powder. Moreover, peaks from α-ZrO_2 disappears with applying spark plasma sintering. This result implies that ZrO_2 powder was completely decomposed into Ti matrix during spark plasma sintering.

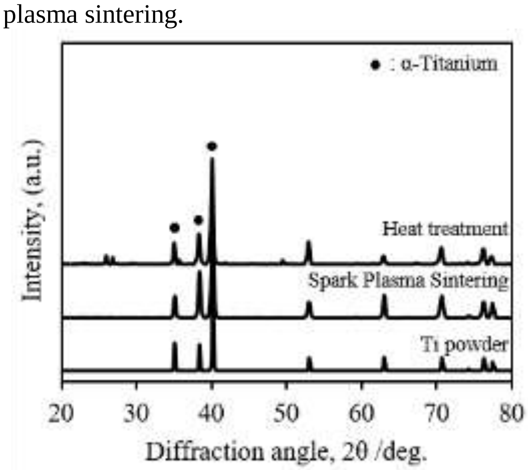

Fig. 2 XRD pattern of Ti+0ZrO_2

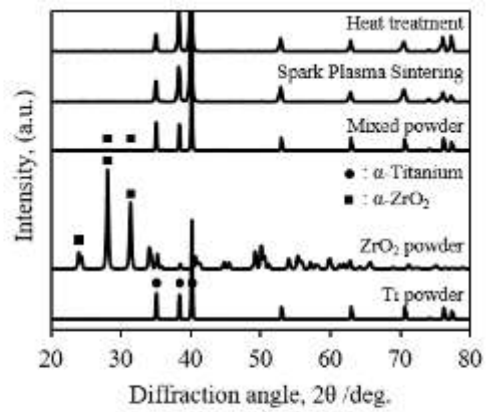

Fig. 3 XRD pattern of Ti+1ZrO_2

Narrow diffraction angle scanning of XRD tests between 68° to 78° were performed to ensure that ZrO_2 powder dissolved into Titanium matrixes. It is obvious from Fig. 4 that, peak of α-Titanium shifted to the lower angle with addition of ZrO_2 powder. According to the Bragg’s equation, it is able to understand that there are some foreign atoms inside Titanium matrixes, which resulting in extending of the c-axis. From Fig. 5, c-axis and a-axis values were calculated from XRD data. The increment of c-axis value came from the addition of ZrO_2 powder. As a result, ZrO_2 completely decomposed into Zirconium and Oxygen after spark plasma sintering followed by heat treatment. In addition, no precipitates or compounds were confirmed.

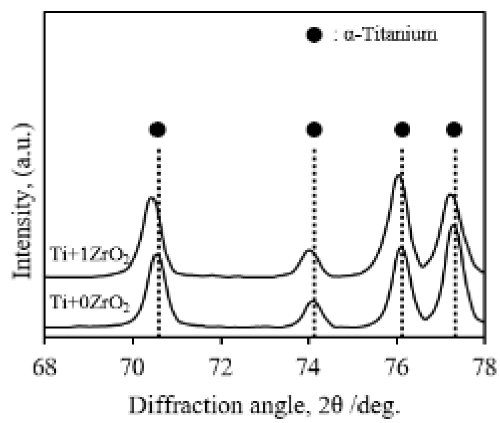

Fig. 4 Comparison of the XRD pattern of Ti+ZrO_2 alloys

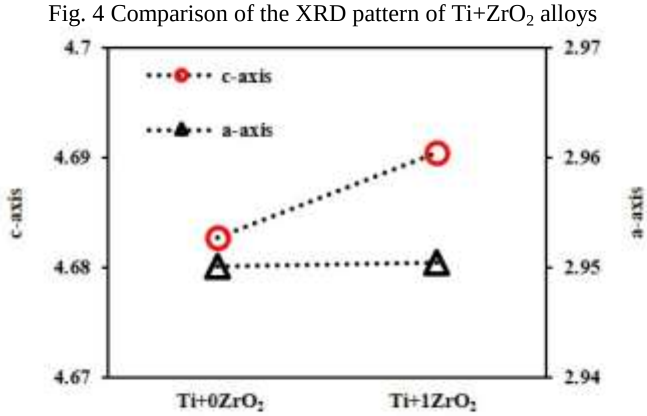

Fig. 5 Lattice constants of c-axis and a-axis of Ti+0ZrO_2 and Ti+ZrO_2 after hot extruded at 850°C

According to the optical microstructures in Fig. 6, fine α-Titanium grain with the size approximately 8 μm of Ti+ZrO_2 after heat treatment and hot extrusion were observed. It is obvious that small amount of additional ZrO_2 powder do not affect both the size and shape of α-Titanium grain. Whereas the result from Vickers hardness test (HV) in Table II, pointed that the increment of ZrO_2 powder significantly improve the hardness of Ti+1ZrO_2 due to the solid solution strengthening from both Zirconium and Oxygen inside the Titanium matrixes as substitutional and interstitial, respectively.

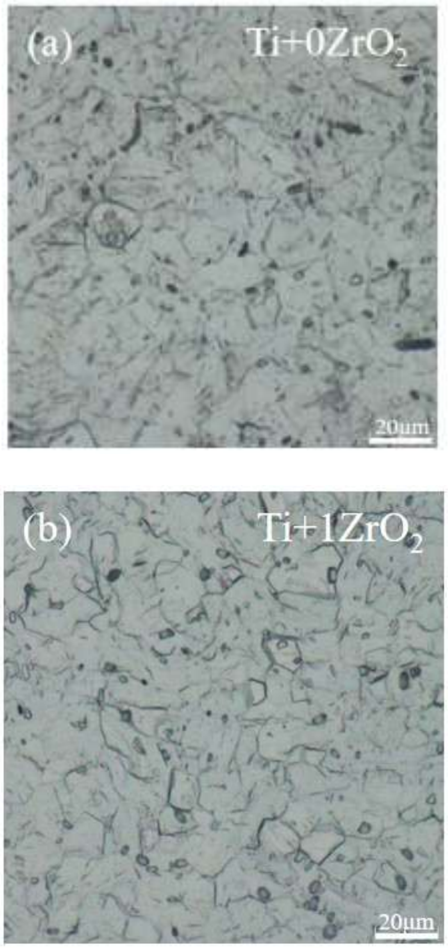

Fig. 6 Optical microstructures of (a) Ti+0ZrO_2, hot extruded at 850℃, (b) Ti+1ZrO_2, hot extruded at 850℃

In powder metallurgy, porosity is one of the main factors which directly affect the mechanical properties [12] since those residue pores act as a stress concentration, lead to crack initiation and propagation. Relative density measurements were performed to observe those residue pores, as shown in Table II. Both Ti+0ZrO_2 and Ti+1ZrO_2 reveals similar relative density of 100%, indicates that there are no residue pores inside. Furthermore, Oxygen and Nitrogen content should be accounted carefully since small amount of these interstitial elements could significantly affect mechanical properties. According to Table II, the increment of Oxygen content in Ti+1ZrO_2 is nearly equivalent to theoretical value of the additional 1 wt% ZrO_2 powder. Whereas Nitrogen content remains the same in both conditions.

TABLE II: CHARACTERISTICS OF HOT EXTRUDED Ti+ZrO_2

Condition	Relative density	Hardnes s (Hv)	Oxygen content (wt%)	Nitrogen content (wt%)
Ti+0ZrO_2, extruded at 850℃	100%	244	0.2933	0.0235
Ti+1ZrO_2, extruded at 850℃	100%	321	0.5347	0.0205

Mechanical properties of hot extruded Ti+ZrO_2 specimens were evaluated by universal tensile test as demonstrated in Fig. 7. Ti+0ZrO_2 exhibits 0.2% offset yield strength, tensile strength and elongation at 466.5 MPa, 630.5 MPa and 35.7%, respectively. Whereas Ti+1ZrO_2 exhibits 0.2% offset yield strength, tensile strength and elongation at 722.9 MPa, 858.6 MPa and 33.7%, respectively. The increment of strength mainly caused by the addition of ZrO_2 content due to the solid solution strengthening of Zirconium and Oxygen as previously discussed. Apart from significantly increment of the strength, it is found that there is almost no change in the elongation of Ti+0ZrO_2 and Ti+1ZrO_2 after hot extrusion. Since Zirconium and Oxygen did not form the precipitates or compounds with Titanium as those crystal structures were not found in XRD results. However, with the increment of Oxygen content from the additional of ZrO_2 powder, this result goes against another report [13] where elongation should be decreased. Further investigation on the grain orientation and texture of material should be conducted in order to understand this phenomenon.

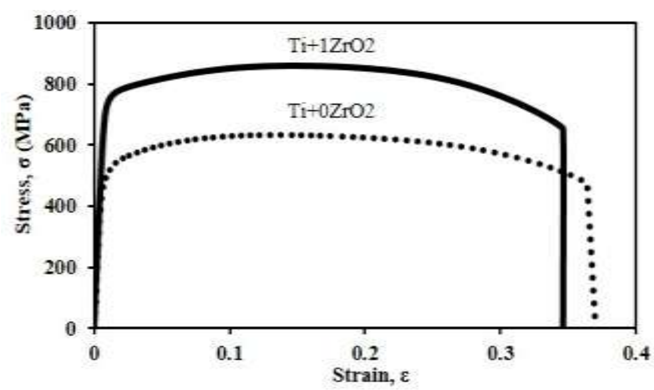

Fig. 7 Stress-strain curves of Ti+ZrO_2, hot extruded at 850℃

IV. CONCLUSION

1) Additional ZrO_2 powder was decomposed and solid soluted in Titanium matrixes during the solid-state sintering by SPS process at temperature of 1100℃ for 3 hours under compressive pressure at 30 MPa in vacuum condition followed by heat treatment at temperature of 1000℃ for 3 hours.
2) Increment of the mechanical properties mainly caused by the solid solution strengthening after the decomposition of ZrO_2 powder. Additional 1 wt% of ZrO_2 powder increased hardness, 0.2% offset yield

strength and tensile strength by 31.5%, 55% and 36%, respectively.

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