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Microstructure, Mechanical Property and Biocompatibility of Porous Ti-Nb-Zr Alloys Fabricated by Rapid Sintering using Space Holder

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Space holder method can easily control Young's modulus due to control the pore size, distribution and shape. In this study, porous Ti-Nb-Zr biomaterial which is not included poison elements was successfully fabricated by powder metallurgy using space holder of NH_4HCO_3 and foaming agent of TiH2. The consolidation of powder was conducted by spark plasma sintering process (SPS) at 850 °C under 30MPa conditions. The effect of space holder contents on pore size and distribution of Ti-Nb-Zr alloys was observed by optical microscope (OM) and scanning electron microscope (SEM). As a result of microstructure observation, a lot of pore was uniformly distributed in the sintered Ti-Nb-Zr alloys. Cell cultivation experiments were conducted using cell cultivation experimental. The porous Ti-Nb-Zr alloys were fabricated successfully with 30% pore ratio and 50-60GPa of Young's modulus. Biocompatibility of porous Ti-Nb-Zr alloys is similar to Ti-6Al-4V alloy.

Keywords: Young's modulus, Biomaterials Scanning electron microscope.

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1. INTRODUCTION

Nowadays, pure titanium, Ti-6Al-4V ELI (extra low interstitial) alloys coated with hydroxyapatite(HA) have been widely used as dental and orthopedic implants [1, 2]. However Al and V toxic elements [3] in Ti-6Al-4V ELI alloys has been considered because of expose into body solution because HA peeled off during usage for long time. There are some problems of the solid implant materials in orthopedic surgery, such as lack of osteointegration capacity and inadequate mechanical properties of Young's modulus. The mismatch of Young's modulus between the bone (2–20 GPa) and the metallic implants of pure Ti and Ti-6Al-4V ELI alloy (100-120GPa) is about 100 GPa [4]. Therefore, it is an important for biometallic materials to have low Young's modulus. Porous metallic biomaterials are one of the methods to reduce the Young's modulus.

In this study, space holder (NH_4HCO_3) was used to make porous Ti-Nb-Zr alloy. During sintering, space holder was removed and pores in Ti-Nb-Zr alloy were formed. It is possible to make pore volume fraction of 60~80%[5)] by the space holder volume fraction.

In this study, porous Ti-Nb-Zr alloys were fabricated by using Ti , Nb and Zr high energy mechanical milled powders with space holder of NH_4HCO_3 with foaming agent of TiH_2. And then these mixed and milled powders were sintered by SPS.

2. EXPERIMENTAL

The raw powders of high purity Ti (99.9%. 100μm), Nb(99.9%, 120μm), Zr(99.8%, 100μm), TiH_2(99%10μm) and pure NH_4HCO_3 powder (120~200 μm) were used to make Ti-13wt%Nb-13wt%Zr-10wt%NH_4HCO_3-2wt%TiH_2 powders. Ti-13wt%Nb-wt%Zr alloy powders were mixed for 24h using a low energy mixing equipment with a ball to powder ratio of 7:1, and milled for 4, 8 and 12h by high energy mechanical milling (HEMM) equipment. And then 10wt%NH_4HCO_3 and 2wt%TiH_2 added in the mixed and milled Ti-13wt%Nb-wt%Zr alloy powders. Then Ti-13wt%Nb-13wt%Zr-10wt%NH_4HCO_3-2wt%TiH_2 powders were mixed for 1h using mixer without ball. The powders were placed in a 10mm-diameter cylindrical graphite die of the SPS equipment. The microstructure and phases of as mixed and as milled powders and the sintered biomaterials were investigated using scanning electron microscope (SEM; JMS-6400), X-ray diffraction (XRD) with Cu-Kα radiation within the range of 20-80°. The pore size and distribution were observed by SEM.

Compressive test was conducted using compressive test machine(Shimazu UH-F50A). Cell cultivation method was used to evaluate biocompatibility.[6)]

3. RESULTS AND DISCUSSION

Fig. 1 shows SEM micrographs of the mixed and milled Ti-13wt%Nb-13wt%Zr alloy powders with10wt%NH_4HCO_3-2wt%TiH_2 powders. The particle sizes of the composite powders decreased from 20~40μm (Fig. 2b, 2c) to less than 5~20 μm (Fig. 2d) with increasing milling time. And the shape of the milled powders changed from an irregular shape to a round shape. The shapes of space holder (NH_4HCO_3) were kept as round shape because the Ti-13wt%Nb-13wt%Zr powder with 10wt%NH_4HCO_3-2wt%TiH_2 composite powders didn't milled due to keep size and shape of the space holder.

By the XRD analysis results of the sintered Ti-13%Nb-13%Zr alloys with 10wt%NH_4HCO_3-2wt%TiH_2 using mixed and high energy mechanical milled Ti-13wt%Nb-13wt%Zr alloy powders show that α-Ti phase was remained in all sintered specimens except a Ti-13wt%Nb-13wt%Zr alloys sintered by SPS using 12h milled powder, but its diffraction intensity of α-Ti

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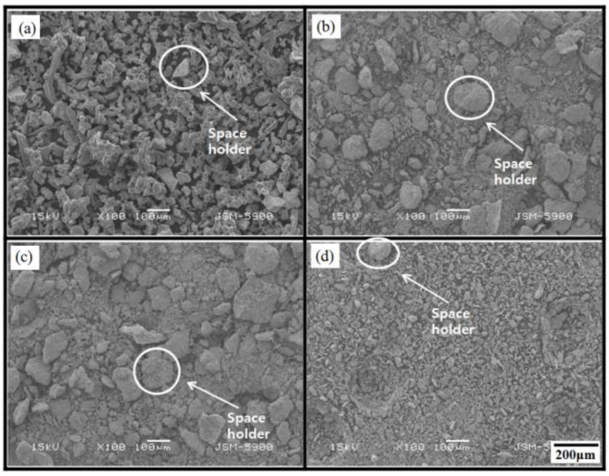

Fig. 1 – SEM micrographs of the Ti-13%Nb-13%Zr alloy powders mixed for 24h or milled for 4-12h and followed by mixed with 10%NH_4HCO_3-2%TiH_2 for 1h using mixer; (a) 24h mixed, (b) 4h milled, (c) 8h milled and (d) 12h milled Ti-13%Nb-13%Zr powder.

phase was relatively decreased with increasing milling time. Furthermore, β-Ti phase was formed by transformation of α-Ti phase in 12h milled specimen due to ultra fine grains. And other reasons are increase of defects such as grain boundary, dislocation and vacancy and increase of grain boundary energy due to high energy mechanical milling. These defects and ultra fine grains increased diffusion rate of transformation from α-Ti phase to β-Ti phase. Ammonium hydrogen carbonate (NH_4HCO_3) evaporates at below 200 ˚C as an ammonia, carbon dioxide and water [5]. For this reason, pores were formed by evaporate space holder during sintering at 850 ˚C.

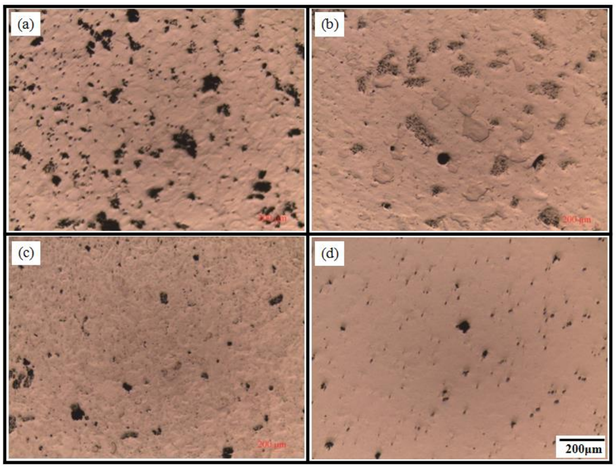

Fig. 2 – OM micrographs and area percent of pores of the sintered Ti-13%Nb-13%Zr-(10%NH_4HCO_3-2%TiH_2) ; (a) 24h mixed, (b) 4h milled, (c) 8h milled and (d) 12h milled.

Fig. 2 shows OM micrographs of the sintered Ti-13%Nb-13%Zr alloys with 10wt%NH_4HCO_3-2wt%TiH_2. From the result of image analysis using image analyzer (Image Pro Plus), the pore ratio of (a), (b), (c) and (d) was 21.74, 10.42, 8.36, 5.6 %, respectively. The pore size decreased from 120~170μm in 24 mixed specimen to 20~50μm in 12h milled specimen (d) using ultra fine Ti-13%Nb-13%Zr milled powder with a pressure (30MPa) during sintering. This is because fine milled particles partially filled pores formed by during sintering at low temperature.

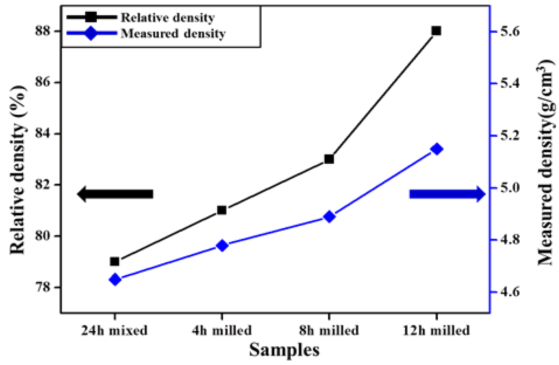

Fig. 3 – The density of relative and measure of the sintered porous Ti-13%Nb-13%Zr alloys.

Fig. 3 shows compressive strength and Young's modulus of the sintered Ti-13%Nb-13%Zr alloy with 10%NH_4HCO_3-2%TiH_2 using mixed and milled powder. With increase milling time, compressive strength was increased as 923, 1166, 1229, 1540 MPa respectively, and Young's modulus was increased as 51, 52, 58 and 78 GPa. From these results, elastic modulus of porous Ti-Nb-Zr alloys was similar to bone, but it is obtained a higher elastic modulus of the sintered porous Ti-Nb-Zr alloys using 8h, 12h milled powder than bone. Is a result of using the 10% space holder and ultra fine particles formed by high energy mechanical milling (HEMM). Therefore adjusting the amount of space holder, it is possible to make biomaterials similar to elastic modulus of bone.

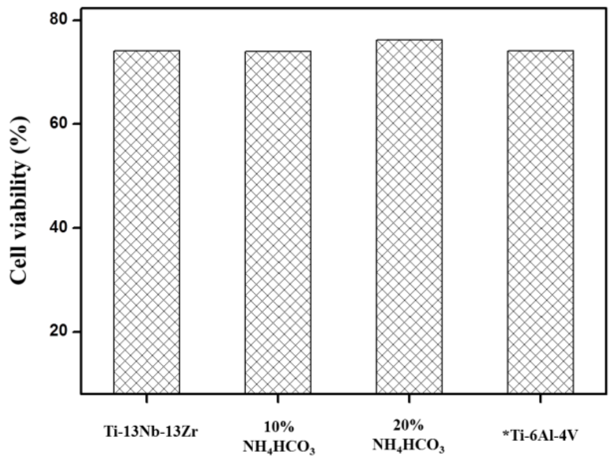

Fig. 4 – Results of cell viability of the Ti-Nb-Zr composites and Ti-6Al-4V alloy.

The result of cell viability of the sintered porous Ti-Nb-Zr alloys and Ti-6Al-4V ELI alloy is shown in Fig. 4. Cell viability result indicating the amount of the viable cells on the samples was obtained using an ELISA leader. This result showed that the biocompatibility of porous Ti-Nb-Zr alloys was similar to the commercial Ti-6Al-4V alloy. In case of porous Ti-Nb-Zr alloys, it showed higher biocompatibility with increasing contents of space holder.

4. CONCLUSIONS

In this study, the effects on the mechanical properties and pore characteristics of biomaterials by spark plasma sintering using space holder were examined.

1. Having the low Young's modulus of 51, 52 and 58GPa, porous Ti-Nb-Zr biomaterial with space holder (NH_4HCO_3) and pore foaming agent (TiH_2) were successfully fabricated by SPS using 4 and 8h high energy mechanical milled powders and 24h mixed powders.
2. The pore ratio was decreased with increasing milling time. The size of pore of the sintered specimen using 12h milled powder was decreased up to 20~50μm during sintering.
3. The compressive strength and Young's modulus was increased with milling time, because of grain size of sintered alloys were decreased with increasing milling time.
4. Biocompatibility of porous Ti-Nb-Zr alloys is similar to Ti-6Al-4V alloy.

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