MECHANICAL PROPERTIES AND BIOCOMPATIBILITY OF Ti-Nb-X-HA COMPOSITES FABRICATED BY RAPID SINTERING USING HIGH ENERGY MECHANICAL MILLING POWDERS

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1. Introduction

Ti-6Al-4V ELI alloys have been widely used as alternative bone because of its excellent biocompatibility, although it still has many problems such as high elastic modulus and toxic. Therefore, biomaterial with low elastic modulus and nontoxic has to be developed. In order to overcome these problems, new Ti based alloys with non-cytotoxic containing biocompatible elements such as Nb, Zr, Ta, Sn, Mo, and Si have been developed [1]. Recently, β-titanium alloys, Ti-Nb, Ti-Ta, and Ti-Zr based alloy systems, have been to achieve both lower elastic modules and better biocompatibility than Ti-6Al-4V ELI alloys.

Hydroxyapatite (HA) has received considerable attention as materials for dental implants because it directly bond with human bone.

Also, HA has good biocompatibility and osteoconductivity. It is now commonly used by applying plasma-sprayed HA coating on the surface of titanium and titanium alloys. However, the HA coating has a tendency to degrade and peel off from the titanium alloy substrate after implantation [2].

In this study, Ti-Nb-(Zr/Si)-HA composites were fabricated by spark plasma sintering (SPS) using various milled powder for 1h, 4h, and 6h for improving mechanical property.

2. Experimental procedure

The raw materials were milled in a mixing machine (24h) and a plantary mechanical ball milling (1h, 4h and 6h) respectively. Ti-Nb-X(Zr,Si)-HA composites were fabricated by SPS at 1000˚C under 70MPa using mixed and milled powder. The phase of Ti-Nb-(Zr,Si)-HA composites and powders were investigated using X-ray diffraction (XRD) with CuKα radiation within the range of 20-80˚. The shape of Ti-Nb-(Zr,Si)-HA powders and morphologies were observed by a scanning electron microscope (SEM). The density of the sintered Ti-Nb-(Zr,Si)-HA composites was calculated by Archimedes' method. The hardness of the sintered specimens was measured using Vickers hardness machine.

For the biocompatibility test, cell cultivation experiment was performed. The sintered composites were placed in a 24-well plate. And $5x10^4$ cells were attached on the sintered composites under a 5% CO_2 atmosphere and held in an incubator for 72h. 100μl of MTT (Tetrazlium-based colori metric) solution was used to distinguish between the cultivated cell and sintered composites followed by holding for 4h. The surviving cells were counted by ELISA (Enzume-Linked Immuno Sorbent Assay) leader.

3. Results of discussion

Fig.1 shows SEM images of mixed and milled Ti-26%Nb-1%Si-10%HA powders. As shown in Fig. 1, the average particle size of the powder decreased with increasing milling time. The shape of the powder particles also changed from plate-like to spherical shape. During high energy mechanical milling (HEMM), particles agglomerated by cold welding and were broken by collision between steel balls. This process continued during HEMM.

Fig.2 shows SEM images of the sintered Ti-26%Nb-1%Si-10%HA composites. As shown in Fig. 2, ratio of pore was decreased with increasing milling time,

and microstructure of 6h milled specimens was finer than that of 24h mixed specimen.

Fig.3 shows the XRD pattern of Ti-Nb-Zr-HA composites fabricated by SPS and different milled powder. The XRD patterns show that α-Ti phase still remained in all sintered specimens. But α-Ti phase was reduced gradually with increasing milling time and α-Ti phase in the specimen fabricated by 6h milled powder almost disappeared. At same time, β-Ti phase was formed from α-Ti phase. Because, by the addition of Nb in Ti alloy promotes phase transformation of α-Ti phase to β-Ti phase. XRD pattern showed Ti_2O, CaO, $CaTiO_3$, and Ti_xP_y formed by chemical reaction during sintering. These phases indicate that HA would react with Ti during sintering process. And this reaction has been found in many Ti-HA bio-composites [3].

Table 1 shows the hardness of sintered Ti-Nb--(Zr,Si)-HA composites using mixed and milled powder. The hardness of sintered composites increased with increasing milling time and by the addition of HA. Some papers have been reported that hardness of the sintered composite fabricated by milled powder depends on the milling time, because grain size of the sintered composites decreased with increasing milling time [4]. And HA is higher hardness, so the Ti-Nb-Si-HA composite shows higher hardness than Ti-Nb-Si composite.

Fig. 4 shows potentiodynamic polarization curves of the sintered Ti-Nb-,Si)-HA composites. The results of the Tafel extrapolation of the polarization curves are presented in Table 3. Higher corrosion current indicates more rapid corrosion rate of the sample. As shown in Fig. 4 and Table 3, Ti-26wt%Nb-1wt%Si-HA composite fabricated using 6h milled powders has the lowest current density (I_{corr}). And with increasing milling time and by addition of HA content, current density was decreased. Therefore Ti-26%Nb-1%Si-10%HA composite fabricated using 6h milled powder has excellent corrosion resistance. Difference in corrosion tendency between each composite is attributed to the difference in the chemical composition of the sample surface affecting the surface sensitivities such as corrosion and high temperature oxidation rate.

Table 2 shows the results of absorbance cell cultivation. Sintered composites using mixed and milled powders have higher value compared to Ti-6Al-4V ELI alloys [5]. These results suggest that biocompatibility could be more improved by the addition of HA.

4. Conclusions

This study was conducted to observe mechanical property, corrosion resistance and biocompatibility of the Ti-Nb-(Zr,Si)-HA composites fabricated by SPS using mixed (24h) and milled powders (1h, 4h, 6h). The results were summarized as follows.

(1) Particle size of the powders decreased with increasing milling time. The shape of the milled powder particles also changed from needle and plate-like to spherical shape. Microstructure of the sintered composites became finer with increasing milling time.

(2) Ti-Nb-(Zr,Si)-HA composites can be soundly fabricated by SPS using HEMM powder.

(3) New phases, Ti_2O, CaO, $CaTiO_3$, and Ti_xP_y were formed during sintering.

(4)Hardness was increased with increase milling time. And also hardness of composites increased by the addition of HA.

(5) Corrosion resistance and biocompatibility of the Ti-26wt%Nb-1wt%Si composite increased with increasing milling time and by the addition of 10wt%HA.

Acknowledgments

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References

[1] E.Takahashi, T. Sakurai, S. Watanabe, N. Masahashi, and S. Hanada “Mater. Trans”. 43, 2978, 2002.

[2] E.H Kim, Y.C kim, S.H Han, S.J Yang, J.W Park, and H.K Seok “J. Kor. Inst. Met. & Mater.” Vol. 47, No1, pp 13~20, 2009.

[3] C.Q.Ning, Y.Zhou, Biomater. 23, 2909 (2002)

[4] J. W. Song, H. S. Kim, H. M. Kim, T. S. Kim and S. J. Hong “J. Kor. Power Met. Int.”

[5] W. D. Woo, H. B. Lee, I. Y. Kim, I. J. Shon, and D. L. Zhang “Met. & Mat. Int.”. Vol. 14, No. 3, pp 327-333, 2008.

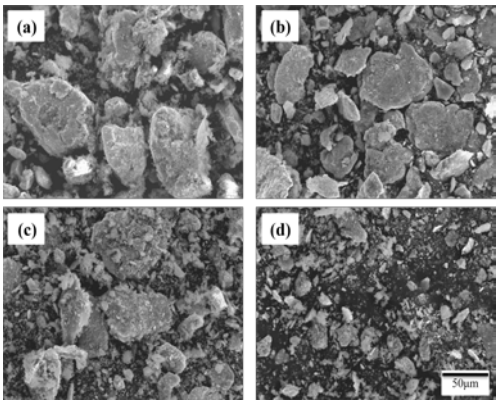

Fig.1. SEM images of the sintered Ti-26%Nb-1%Si-10%HA powder; (a) 24h mixed, (b) 1h milled, (c) 4h milled and (d) 6h milled.

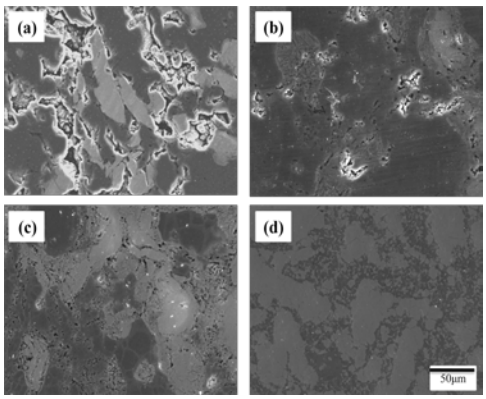

Fig.2. SEM images of the sintered Ti-26%Nb-1%Si-10%HA composite; (a) 24h mixed, (b) 1h milled, (c) 4h milled and (d) 6h milled.

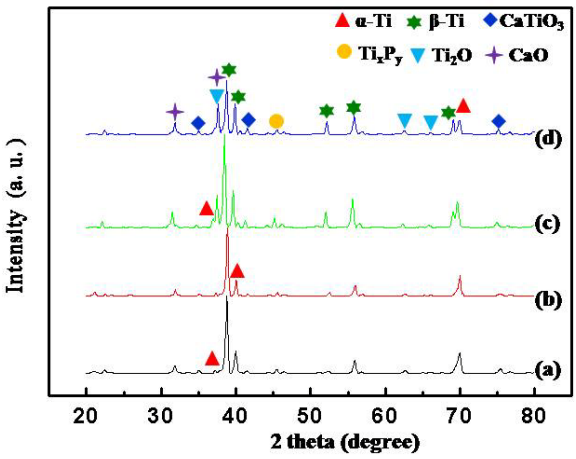

Fig.3. XRD patterns of the sintered Ti-35%Nb-7%Zr-10%HA composite; (a) 24h mixed powder, (b) 1h milled powder, (c) 4h milled powder and (d) 6h milled powder.

Table 1. Vickers hardness of the sintered composites (HV)

	Ti-35% Nb-7%Zr	Ti-35%Nb -7%Zr-10%HA	Ti-26% Nb-1%Si	Ti-26%Nb-1%Zr-10%HA
Mixed 24h	297.6	602.1	335.1	615.8
Milled 6h	897.1	901.4	701.8	936.3

Table 2. Results of absorbance cell cultivation

	Ti-35% Nb-7%Zr	Ti-35%Nb -7%Zr-10%HA	Ti-26% Nb-1%Si	Ti-26%Nb-1%Si-10%HA
Mixed 24h	0.18	0.43	0.17	0.30
Milled 6h	0.22	0.69	0.22	0.47

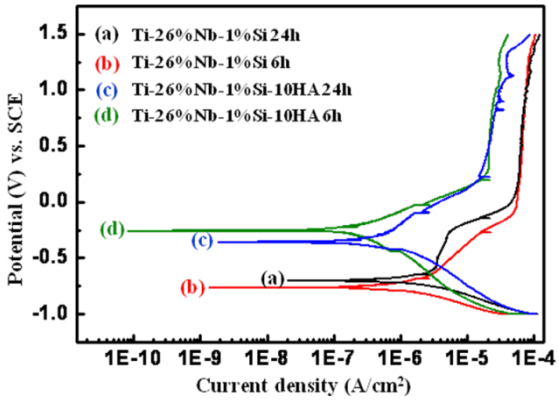

Fig.4. Potentiodynamic polarization curves of the sintered Ti-Nb-Si-HA composites.

Table 3. The result of potentiodynamic polarization test

Samples	(a)	(b)	(c)	(d)	Ti6Al 4V
I_{corr}(μA)	32	28.9	12.6	8.2	17.0
E_{corr}(mV)	-706	-763	-359	-252	-573.3

*Ref. [5]