Effects of Magnesia Particle Addition on Mechanical and Bioactive Properties of Magnesia/Titanium Composite

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In order to develop new titanium matrix composite for surface-coating titanium used in biomedical field, magnesia particles were added into pure titanium through hot press sintering method. Samples fabricated at the temperature of 973 K and at the pressure of 55 MPa were used to investigate the effects of magnesia addition on the properties of the new composite. In the fabricated samples, uniform dispersion of magnesia particles in titanium matrix was successfully obtained and no reaction layer was observed at interface between magnesia particles and titanium matrix. The volume fraction (V_f) and the size of magnesia particles mainly influenced tensile strength of the samples. When the size of magnesia particles was in the range of 25–90 μm , tensile strength of the composite was increased with increase of V_f till 5%. With respect to biocompatible property, the results of simulated body fluid immersion test showed that an apatite surface layer was formed on the fabricated magnesia/titanium composite samples, which would be benefit to bonding of the material to surrounding bone when it would be implanted into human body.

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1. Introduction

The properties of titanium medical implants with surface coating layer are greatly related to the properties of coated layer material and the process for coating surface layer onto titanium substrate. Through the bioactivities of surface layer material, the bonding of implants with the surrounding tissues is enhanced and the fixing strength of implants with the living tissue is decided by the bioactivities of layer material.

The most often used bioactive coating material is hydroxyapatite (HAP). Because the inorganic and crystallographic components of HAP is similar to that of living bones, hydroxyapatite layers can lead to direct bonding or earlier stabilization of implants with the surrounding bones or tissues.^{1–3)} However, due to the HAP's limited mechanical properties, some mechanical failure of prostheses with coated HAP layer has been reported after long-term implantation. Therefore, some new bioactive layer materials have become research topic. These materials include bioactive glass (BAG),^{4–6)} amorphous hydrogenated carbon (a-C: H),⁷⁾ and bio-composites (BC).⁸⁾ The BAG is consisted of a family of glass compositions, which can be bound in a few hours to hard and soft tissue, therefore shows a good bioactive behavior. The hydrogenated carbon (a-C: H) not only shows good biocompatibility but also possesses chemical inertness, low coefficient of friction and high wear resistance, which protect implants from formation of wear particles and release of metal ions. The BC is mainly consisted of two kinds of components; one is mechanical strong but bio-inert and another is bioactive but mechanically poor.

In addition to bioactivity, the bond strength of a coating layer with the metal substrate is also very important. If the layer is separated from implant during actual application, the detached fragments enhance the friction between implants and surrounding bones and subsequent release of inflamma-

tory mediators, which stimulates prosthesis loosening due to osteolysis. Therefore various techniques such as sputtering, electron beam depositing, laser depositing, plasma spraying, ion beam depositing, and sintering have been employed to coat surface layer onto substrate.^{9–11)}

The aim of this research is to develop titanium matrix composite used as a surface-coating layer in sintering bonding process. Due to the titanium in the surface layer bridging to the substrate titanium, the bonding strength of the interface between the composite surface layer and the substrate titanium is higher than that formed by other methods. In the previous paper,¹²⁾ the preparation of HAP/Ti composite coatings by sintering bonding method has been investigated. In the present paper, magnesia used as a replacement of HAP is added into titanium matrix through sintering method considering that mechanical properties of magnesia are more excellent than that of HAP. The bioactivity of new composite coating materials is investigated by simulated body fluid (SBF) immersion test. The effects of size and volume fraction (V_f) of the magnesia particles on mechanical properties of the composite material are also investigated.

2. Experimental Procedure

Micrograph of magnesia particles (–200 μm , Shinagawa Renga, Ltd.) used in this study is shown in Fig. 1. The shape of magnesia particles was irregular and there were more sharp edges in small particles than in larger ones. The magnesia particles and pure titanium powders (–44 μm) were mixed with kerosene and the magnesia volume fraction of the mixture was changed from 3% to 20%. The mixture was compacted in a cylindrical graphite die (outer diameter: 40 mm, inner diameter: 20 mm) and pressed by a pair of graphite punches (diameter: 20 mm) from both top and bottom of the die. Then it was hot-pressed under vacuum condition in a furnace, which

could produce a rapid resistance heating by the direct current through punches. The pressure was kept at 55 MPa during the hot-press and the holding time to 30 min. The temperature was 973 K, which was monitored by an attached chromel-alumel thermocouple. The slices cut from the fabricated titanium composite were mechanically polished using silicon carbide papers and fine polished with diamond pastes (particle diameter 3 μm and 1 μm) for microstructure observation through scanning electron microscopy (SEM) and electron probe microanalyses (EPMA).

The specimens with the gauge length of 10 mm for tensile test were cut from the fabricated titanium composite. The tensile test was conducted under a crosshead speed of

0.083 mm/s at room temperature. For evaluating the bioactivity of titanium composite, whether an apatite (calcium phosphate) layer could be formed on the surface of it in simulated body fluid (SBF)¹³ was used in this study. The samples were soaked in 100 ml of a SBF (pH: 7.25) at 309.5 K for 2 weeks. The ion concentration of the used SBF were Na^+ : 0.142, K^+ : 0.005, Mg^{2+} : 0.0015, Ca^{2+} : 0.0025, Cl^- : 0.1478, HCO_3^- : 0.0042, HPO_4^{2-} : 0.0010, and SO_4^{2-} : 0.0005 (mol/l), which were close to those of human blood plasma. After soaking finished, the apatite precipitation on the sample surface was observed with SEM. The composition of the precipitated surface layer was analyzed by X-ray diffraction (XRD).

3. Results and Discussion

3.1 Microstructure of the magnesia/titanium composite

Typical microstructures of magnesia/titanium composite are shown in Fig. 2. The composite produced in this fashion using magnesia particles with varying size ranges of -25 , -90 , -200 , $90-200$, $25-90$ μm , respectively. The microphotographs in these figures were taken from the direction perpendicular to the hot-press load axis. It can be seen from the microphotographs that the magnesia particles with different size were uniformly distributed in the magnesia/titanium composite for all samples. No interfacial reaction products could be observed with EPMA. As shown in Figs. 2(f), (g), smaller magnesia grains mainly gathered between boundaries of larger titanium grains and the gathering became stronger when V_f was increased or the magnesia particle size was smaller. When the size of magnesia particles was larger than 90 μm , this gathering tendency almost did not appear as shown in Fig. 2(h). This phenomenon can be explained by the concept as following; the small particles are usually adsorbed to the surface of the large particles in the mixed powders before sintering. As a result, the distribution of magnesia particles in titanium matrix is influenced by the size of the magne-

Fig. 1 Micrographs of magnesia particles used for magnesia/titanium composite (MgO -200 μm).

Fig. 2 Typical microstructures of magnesia/titanium composite. (a): MgO -90 μm , $V_f = 5\%$, (b): MgO -90 μm , $V_f = 10\%$, (c): MgO -200 μm , $V_f = 10\%$, (d): MgO -200 μm , $V_f = 20\%$, (e): MgO $90-200$ μm , $V_f = 20\%$, (f) MgO -90 μm , $V_f = 10\%$, (g) MgO -25 μm , $V_f = 15\%$, (h) MgO $90-200$ μm , $V_f = 15\%$.

sia particles and the sintering of titanium matrix is inhibited by the adsorbed smaller magnesia particles.

3.2 Tensile behavior of the magnesia/titanium composite

Curves representing relations of ultimate tensile strength (UTS) with V_f and particle size are shown in Fig. 3. In the curve of 2–5, tensile strength increased with increasing of V_f of the magnesia particle up to 5%, and after that, it decreased with increasing of V_f of the magnesia particle. In the curve 1, in which $-25\text{ }\mu\text{m}$ magnesia particles were added, the UTS was decreased with addition of magnesia particles at all V_f .

In the curve 5, in which $25\text{--}90\text{ }\mu\text{m}$ magnesia particles were added, the highest UTS was reached at 730 MPa , which was approximately 30% higher than that of pure titanium (about 520 MPa). In the curve 4, in which larger than $90\text{ }\mu\text{m}$ particles were added, the maximum value of tensile strength was almost the same as that in curve 5. However, the minimum value of the UTS at 20% V_f was a little lower than that in curve 5. In curve 2 and 3, in which $-90\text{ }\mu\text{m}$ and $-200\text{ }\mu\text{m}$ magnesia particles were added, the maximum value of UTS was also almost the same as that in curves 4 and 5. However, the minimum values of the UTS at 20% V_f were much lower than that in curve 5.

The main effects of magnesia particle addition on tensile behavior of the composite are considered to be as strengthening, damage of magnesia particles and sintering inhabitation of the titanium matrix. Usually, the strength of composite is decided by the comparative contributions of these three factors. The damage of larger magnesia particles is often stronger than that of smaller magnesia particles and the larger magnesia particle size is, the stronger the damage is.

The strengthening is resulted from the reinforcement magnesia particles, which resist the dislocation slipping or fix the dislocation in titanium matrix. As a result of this plastic flow constraint in the matrix, the internal stress in the matrix is generated. The analysis results^{14–18)} of the internal stress for some particulate reinforcement metal matrix composites show that the internal stress is influenced by the volume fraction and the size of reinforcement particles. With an increase in the particle volume fraction, the internal stress increases and at a given particle volume fraction, the internal stress decreases with an increase in particle size.

In the curve 5, because magnesia particle size was in a suitable range, the UTS was strengthened by the stronger dislocation strengthening effect. However, the effects of magnesia particle damage and sintering inhabitation of the titanium matrix were stronger than the dislocation strengthening effect after the magnesia particle V_f being larger than 5%. Therefore, the UTS was decreased with increase of magnesia particle V_f . Because the magnesia particles damage effect was increased with increase of magnesia particle size, the UTS in curve 4, in which coarser magnesia particles were included, was lower than that in curve 5 after magnesia particle V_f being larger than 5%.

In the curve 1, the easy gathering of finer magnesia particles at boundaries of the titanium grains inhabited the coalescence of titanium grains. Because of this stronger inhabitation effect, the tensile strength of the composite was smaller than pure titanium and it decreased with increase of magnesia particle V_f . Although finer magnesia particles ($-25\text{ }\mu\text{m}$) were in-

Fig. 3 Effect of the volume fraction and size of magnesia particles on the tensile strength of magnesia/titanium composites.

Fig. 4 The fracture surfaces of magnesia/titanium composite after tensile test. (a): MgO $25\text{--}90\text{ }\mu\text{m}$, $V_f = 5\%$, (b): MgO $-90\text{ }\mu\text{m}$, $V_f = 10\%$, (c): MgO $-200\text{ }\mu\text{m}$, $V_f = 10\%$, (d): MgO $90\text{--}200\text{ }\mu\text{m}$, $V_f = 10\%$, (e): MgO $-90\text{ }\mu\text{m}$, $V_f = 10\%$, (f): MgO $-200\text{ }\mu\text{m}$, $V_f = 10\%$.

cluded in the curve 2, the inhabitation effect was weaker than that in curve 1 due to the lower percentage of finer magnesia particles compared to that in curve 1. Therefore, the UTS in curve 2 was larger than that in curve 1 and the variation of UTS with magnesia particle V_f was similar to that in curve 4 and 5, but different from that in curve 1. In curve 3, because

Fig. 5 The surface photographs of pure titanium and magnesia/titanium composite samples soaked in SBF for 14 days. (a): MgO $-200\text{ }\mu\text{m}$, $V_f = 5\%$, (b): MgO $-90\text{ }\mu\text{m}$, $V_f = 5\%$, (c): MgO $25\text{--}90\text{ }\mu\text{m}$, $V_f = 10\%$, (d): MgO $90\text{--}200\text{ }\mu\text{m}$, $V_f = 10\%$, (e): MgO $90\text{--}200\text{ }\mu\text{m}$, $V_f = 15\%$, (f), (g): pure Ti, (h): MgO $25\text{--}90\text{ }\mu\text{m}$, $V_f = 5\%$.

the percentage of finer magnesia particles was lower than that in curve 2 but higher than that in curve 4, the UTS was located between curve 2 and curve 4 after magnesia particle V_f being greater than about 5%. Here, the coarser magnesia particles ($> 90\text{ }\mu\text{m}$) damage effect in curve 3 was neglected due to its relative weakness compared to the finer inhabitation effect for convenience of discussion.

The effects of magnesia particle V_f and size can be seen further from the fracture surfaces of tested samples. As shown in Fig. 4, the fracture surfaces of samples with 5% magnesia particles V_f revealed ductile fracture dimples throughout the fracture surface (Fig. 4(a)), which resulted from the deformation and fracture of titanium matrix. The fracture surfaces of samples with 10% magnesia particles V_f showed brittle fracture appearance and a large number of cracked magnesia particles were distributed on the surface (Figs. 4(c) and (d)). The fracture surfaces of samples (MgO: -90 and MgO: $-200\text{ }\mu\text{m}$) with 10% magnesia particles V_f also exhibited typical fragile appearance (Figs. 4(e) and (f)), which resulted from the finer magnesia particle inhabitation effect. This effect led to crack bridging with fatigue crack growth.

3.3 Apatite-forming ability

The SEM photographs of the surface of pure titanium and the magnesia/titanium composite soaked in SBF for 14 days are shown in Fig. 5. Some spherical particles could be found on the surface of pure titanium and the magnesia/titanium composite. The results of XRD analyses confirmed that the spherical particles were crystalline apatite. The shape of the apatite formed on the surface of titanium and composites was the same (Figs. 5(g) and (h)). However, the numbers of apatite formed on the surface of composites was much more than that formed on the surface of pure titanium, and it was increased with the increase of the magnesia particle V_f or decrease of the magnesia particle size (Figs. 5(a) to (f)). When the V_f of magnesia particle was raised to 10%, a continuous layer of crystalline apatite was formed on the surface of compos-

ites (Fig. 5(c)). This result provided evidence that magnesia had an ability to induce apatite precipitation, which would improve the bonding between the titanium biomaterials and living bone.

4. Conclusions

In order to develop new surface-coated layer for coating to titanium, magnesia/titanium composite was investigated. Through microstructure observation, tensile strength tests and simulated body fluid immersion tests, following conclusions were drawn.

(1) The magnesia particles were uniformly distributed in the titanium matrix. No interfacial reaction products could be detected with EPMA. However, the smaller magnesia particles ($-25\text{ }\mu\text{m}$) tended to gather between boundaries of larger titanium grains. In the case of larger magnesia particles were used as the reinforcement, such gathering behavior tended to disappear and when they were larger than $90\text{ }\mu\text{m}$, the gathering almost disappeared.

(2) The tensile strength of samples without smaller ($-25\text{ }\mu\text{m}$) magnesia particles or with some fraction of smaller magnesia particles was increased with increasing of V_f and after V_f being greater than 5%, the strength was decreased with increase of V_f . The tensile strength of samples with all smaller magnesia particles was decreased with increasing of V_f .

(3) The results of simulated body fluid immersion test showed that the added magnesia particles improved the ability to form apatite on the surface of the composite samples, which was considered to be benefit to the bonding between material and surrounding bone.

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