Synthesis of Ti-Based Glassy Alloy/Hydroxyapatite Composite by Spark Plasma Sintering

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The spark plasma sintering process has been used to fabricate Ti40Zr10Cu36Pd14 glassy alloy/hydroxyapatite composites. XRD, DSC, SEM and compression tests were used to examine the microstructure and properties of the composites. No crystallization was observed in the glassy alloy matrix. The glass transition temperature (Tg) is independent of the HA addition and the onset temperature of crystallization (Tx) slightly decreases with increasing HA content. The sintered composite exhibited reduced value of Young’s moduli as compared with the as-cast Ti40Zr10Cu36Pd14 bulk glassy alloy. [doi:10.2320/matertrans.MBW200716]

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1. Introduction

Since bulk glassy alloys were synthesized for the first time by a copper mold casting process in the late 1980’s,1 a number of bulk glassy alloys in Mg-, La-, Zr-, Pd-, Ti-, Fe-, Co-, Ni- and Cu-based systems have been developed.2 Unique properties of bulk glassy alloys make them extremely attractive for biomedical applications. Recently, bulk glassy alloy composites have attracted much attention due to their improved characteristics. Most of researches for bulk glassy alloy composites have been focused on the improvement of mechanical properties, especially for ductility.3–5

Hydroxyapatite (HA), which is a main mineral constituent of teeth and bone, has an excellent biocompatibility with hard tissue, skin and muscle tissue. Moreover, HA does not exhibit any cytotoxic effects and can directly bond to human bone.6–8 A number of studies have been reported on HA coating on Ti metal and Ti-alloys for improving the surface bioactivity.9–12 However, the HA coatings often flake off as a result of poor bonding at the ceramic/metal interface.13 The problems mentioned above may be solved by fabrication of metal/HA composites. Some papers have been published on the preparing of Ti/HA composite materials.14–16

As a novel rapid sintering technique, the use of a spark plasma sintering (SPS) technique enables the sintering of high quality materials within a short time by controlling the spacing between powder particles, electrical energy and sintering pressure. The SPS includes various phenomena:17 (a) electrical breakdown of surface oxide film and removal of contaminated layer on particle surface by spark generation and sputtering effect; (b) destruction of surface oxide film and neck formation between powder particles; (c) focused current and Joule heat at the neck; and (d) enhanced migration of atom or ion by the difference in temperature between neck and particle core as well as by electrical field, and neck growth. The phenomena provide advantages which cannot be obtained using the conventional sintering process. Consequently, the SPS can be applied to materials which are required to suppress crystallization and grain growth, such as glassy alloys.17

In the present work, HA was chosen as an appropriate second phase to fabricate the Ti-based glassy alloy/HA composites using the SPS technique.

2. Experimental Procedure

In the present study, a Ti40Zr10Cu36Pd14 glassy alloy was chosen as a base material because of its high glass-forming ability. A bulk glassy alloy rod with a diameter of 6 mm has been obtained at this alloy composition.18 An ingot of the alloy was prepared by arc-melting the mixture of pure elements with purities above 99.9% in an Ar atmosphere. The alloy composition represents the nominal atomic percentage of the mixture. The Ti40Zr10Cu36Pd14 glassy alloy powders were prepared by a high pressure argon gas atomization method, and then classified by a conventional sieving method. The gas atomization process is one of useful methods to fabricate glassy alloy powders in a scale of mass production because of the achievement of rather high cooling rates. The powders with particle diameters less than 63 μm were used for the subsequent experiments. The Ti40Zr10Cu36Pd14 glassy alloy powders were mixed with 12% or 30% HA particles in volume. Figure 1 shows SEM images of Ti40Zr10Cu36Pd14 glassy alloy powders and powder mixture with 30 vol% HA. The glassy alloy powders are spherical while the HA particles are polyhedral. The mixture was compacted into a cylindrical die. The sintering was carried out in a vacuum using a SPS system (Model: SPS-3.20 MK-IV) at 643 K under a sintering pressure of 600 MPa. The heating rate was 50 K/min (from room temperature to 543 K), 10 K/min (from 543 K to 623 K) and 5 K/min (from 623 K to 643 K). The holding time at 643 K was 10 minutes. A uniaxial pressure was applied using top and bottom graphite punches. The sintered samples had a cylindrical shape with a diameter of 15 mm and a height of about 6 mm.

X-ray diffraction (XRD) with a monochromatic Cu Kα radiation was used to examine the glassy structure of the
powders and the sintered samples. Thermal stability was evaluated by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. The microstructure of the sintered samples was examined by scanning electron microscopy (SEM) coupled with an X-ray energy dispersive spectrometer (EDS). Compression tests were conducted by an Instron testing machine under a strain rate of \( \frac{5}{10^{-4}} \) s\(^{-1}\). The samples with a rectangular shape of 2.5 mm in width, 2.5 mm in thickness and 5 mm in height were used.

3. Results and Discussion

Figure 2 shows XRD patterns of the powder mixtures and the sintered composite samples with 12 vol% and 30 vol% HA additions. The XRD patterns of Ti\(_{40}\)Zr\(_{10}\)Cu\(_{36}\)Pd\(_{14}\) glassy alloy powders and pure HA powders are also given in Fig. 2(a) for comparison. The alloy powders without HA additions are characterized to be a single glassy phase, as indicated by a halo diffraction peak without any detectable crystalline peaks. The Ti\(_{40}\)Zr\(_{10}\)Cu\(_{36}\)Pd\(_{14}\) alloy powder keeps a single glassy phase in the size range below 200 \( \mu \)m in diameter (the results are not shown in the present paper). For the powder mixtures and sintered samples, several weak diffraction peaks are superimposed over the broad peak due to the glassy phase. The peaks for these samples correspond to those of HA. With increasing HA content, the diffraction peaks of HA phase become stronger.

Figure 3 shows DSC curves of the Ti\(_{40}\)Zr\(_{10}\)Cu\(_{36}\)Pd\(_{14}\) glassy alloy powders and sintered composite samples with various HA addition.
different HA contents at a heating rate of 0.67 K/s. During heating, all the DSC curves exhibit an endothermic event, characteristic of glass transition to supercooled liquid, followed by exothermic reactions corresponding to crystallization of the supercooled liquid. The samples exhibit several exothermic peaks due to a multi-stage crystallization. The features of the DSC curves are almost independent of the existence of HA phase. The glass transition temperature \( T_g \) and the onset temperature for crystallization \( T_x \) are marked with arrows in Fig. 3. There is no distinct difference in the data on \( T_g, T_x \), and \( \Delta T \) between the as-atomized powder and the melt-spun ribbon.\(^{19}\) Though the \( T_g \) is independent of the HA addition, \( T_x \) slightly decreases with the addition of HA. Thus, the supercooled liquid region becomes narrow slightly by the addition of HA. It was reported that the onset temperature of crystallization of an amorphous alloy refer to the temperature where the crystals begin to precipitate from the amorphous matrix.\(^{19,20}\) Hence, \( T_x \) is closely linked with the nucleation process. S. Venkatarman suggested that the thermal treatment would enhance a short-range order.\(^{21}\) In the present work, the sintering process conducted near the \( T_g \) can result in structure relaxation in addition to possible phase separation. The heterogeneous structure as well as composition changes induced by sintering process is likely to form the nuclei for crystallization. Hence, the onset temperatures of crystallization of composites decrease slightly.

The microstructure of the sintered composite samples is shown in Fig. 4. The \( \text{Ti}_{40}\text{Zr}_{10}\text{Cu}_{36}\text{Pd}_{14} \) glassy alloy powders are coalesced together by the neck formation, as marked with arrows in Fig. 4. It is seen that the HA particles are in a polyhedral shape, and distribute over the whole sintered samples. In the present work, the sintering temperature is 643 K, which is far lower than the crystallization temperature (718 K), even though the glass transition temperature (665 K). The total period, including heating and holding times, is less than 30 minutes. Therefore, the crystallization during sintering is avoided completely, as indicated by XRD patterns. The \( \text{Ti}_{40}\text{Zr}_{10}\text{Cu}_{36}\text{Pd}_{14} \) alloy has high oxidation reaction at high temperatures. Some pre-existing impurities in the melt due to an inadequate vacuum during melting, such as surface oxide film, would suppress the atomic diffusion as well as the neck formation between different particles during sintering. The SPS process is expected to solve this problem because of its unique characters, as mentioned above.

The HA has a poor strength (lower than 150 MPa).\(^{7}\) Thereby, the HA particles are crushed and filled in the residual space among the \( \text{Ti}_{40}\text{Zr}_{10}\text{Cu}_{36}\text{Pd}_{14} \) glassy alloy powders because of the present high sintering pressure (600 MPa). Furthermore, significant deformation of \( \text{Ti}_{40}\text{Zr}_{10}\text{Cu}_{36}\text{Pd}_{14} \) glassy alloy powders is also observed during the sintering process, as shown in Fig. 4. This is due to the viscous flow which can occur at the high temperature above \( 0.7T_g \).\(^{22}\) In the present work, the sintering temperature is 643 K, which is higher than \( 0.7T_g \) (0.7 \( \times \) 665 K = 465.5 K). The viscous flow of the glassy alloy powder causes the reduction of the pores in the sintered samples. The bonding at the interface between glassy matrix and HA particles can be improved through the formation of the protrusion by both crush of HA particles and viscous flow deformation of glassy alloy powders. In the XRD patterns of the sintered composite samples, a halo peak and several crystalline peaks corresponding to the coexistence of glassy and HA phase, are identified. No other peak is observed, indicating that the structure of both HA and glassy alloy powder remains unchanged even after the SPS treatment. In the SPS process, the heat is transferred immediately and diffused to whole glassy alloy powders so that the bonding portion is quickly cooled. It is necessary for good biocompatibility and mechanical properties of the composite to keep the original structure of HA and glassy alloy powder.

Figure 5 shows the compression stress-strain curves of the sintered composite samples. The sample with 12 vol% HA exhibits an elastic elongation of 1.7%. The stress-strain curve deflects from the linear elastic elongation when the strain is over 1.7%. The fracture strain is 2.3%. The compressive strength and the Young’s modulus are 1310 MPa and 65 GPa, respectively. For the sample with 30 vol% HA, the elastic elongation, fracture strain, compressive strength and Young’s modulus are 0.7%, 0.8%, 394 MPa and 55 GPa, respectively.

The compressive strength of the sintered samples decreases with increasing HA content. This is because that the HA phase has lower strength which results from the insufficient densification under the present sintering conditions. In addition, with increasing HA content, the areas of direct

![Fig. 4 SEM micrographs of the sintered samples with 12 vol% (a), and 30 vol% (b) HA.](image-url)
Young’s moduli of traditional metallic biomaterials are at much higher the one of bones (less than 200 MPa). This implies that the sintering composites could meet the strength demand for bone replacement. A problem concerning metallic implants in orthopedic surgery is the significant mismatch of Young’s modulus between the human bone and metallic implants. The bone is insufficiently loaded due to the mismatch, as called ‘‘stress-shielding’’. In general, the compressive strength of the sintered composite samples is slightly decreases with increasing HA content. The sintered composite samples exhibit lower Young’s moduli than those of the as-cast Ti$_{10}$Zr$_{10}$Cu$_{36}$Pd$_{14}$ bulk glassy alloy.

4. Conclusions

A Ti$_{10}$Zr$_{10}$Cu$_{36}$Pd$_{14}$ glassy alloy/hydroxyapatite(HA) composite has been successfully synthesized by the SPS process. No crystallization is observed in the Ti$_{10}$Zr$_{10}$Cu$_{36}$Pd$_{14}$ glassy phase matrix. The glass transition temperature ($T_g$) is independent of the HA addition and the onset temperature of crystallization ($T_x$) slightly decreases.

References