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Formation of Ca–P layer on the Ti-based bulk glassy alloy by chemical treatment

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ABSTRACT

In the present paper, a chemical treatment method has been employed to prepare a bioactive layer on the surface of $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ bulk glassy alloy. Prior to forming an apatite layer, all samples were dipped in mixed acid (HNO_3 and HF) aqueous solution and boiled in 1.2 M NaOH aqueous solution. Then, they were soaked in simulated body fluid (SBF) to form an apatite layer on the surface. The apatite layer was characterized by X-ray diffraction (XRD), X-ray photoemission spectroscopy (XPS) and environment scanning electron microscopy (ESEM). The results show: a dense and uniform calcium phosphate layer mainly composed of HA and $Ca_2P_2O_7$ was rapidly deposited on the pre-calcified $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ bulk glassy alloy in SBF within 7 days.

1. Introduction

Ti-based bulk glassy alloys are expected to be applied as a new type of biomaterials due to their unique mechanical properties (high strength, high hardness, low Young's moduli and high elastic limitation). To date, a number of Ti-based bulk glass-forming alloys, such as Ti–Cu–Ni–(Sn or Sb) [1], Ti–Cu–Ni–Si–B [2,3], Ti–Zr–Ni–Cu–Sn [4], Ti–Cu–Ni–Zr–Al–Si–B [5], (Ti, Zr)–(Cu, Ni) [6] have been synthesized by the copper mold casting method. However, most of the Ti-based bulk glassy alloys have lower GFA. The limited dimensions seriously prevent further extension of commercial applications. Kim et al developed Ti–Zr–Be–Cu–Ni bulk glassy alloys system with critical diameters of 8–10 mm [7–9]. However, the exist of toxic elements Be and Ni restricts the biomedical applications of Ti-based bulk glassy alloys. It is of scientific and technological interest to synthesize new Ti-based bulk glassy alloys free of toxic elements. Recently, we successfully developed the Ti–Zr–Cu–Pd bulk glassy alloy system with critical diameters of 6–7 mm [10,11]. As similar for a number of multicomponent bulk glassy alloys, it is expected that an optimum alloying to more multicomponent system for the Ti–Zr–Cu–Pd alloys causes a further increase in the critical diameter.

As a candidate for implant, the biocompatibility of Ti-based bulk glassy alloys should be considered. Hydroxyapatite (HA) with similar composition and structure as those of human bone has excellent biocompatibility. The formation of HA layer on Ti-alloy surface are effective approach for improving the biocompatibility. In the previous works, we successfully prepared calcium phosphates layers on the surface of NiTi alloy by chemical treatment [12,13]. The calcium phosphates coated NiTi has a better biocompatibility as compared with the mechanically polished NiTi and shows a good osteoconductivity [14,15]. In the present paper, a simple chemical treatment procedure was introduced to treat the Ti-based bulk glassy alloy in order to form the bone-like calcium phosphate coating.

2. Experimental

TiZrCuPdSn alloys system exhibits good glass-forming ability [16]. In the present paper, $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ cylindrical rods with diameter of 5 mm were prepared by copper mold casting. Full glassy structure of the rods was examined by X-ray diffraction meter (XRD, RIGAKU DMAX), as shown in Fig. 1.

$Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ bulk glassy alloy samples with size of Ø 5 mm × 2 mm were employed as substrates. Prior to surface treatment, all samples were abraded with No. 400 diamond plates, cleaned with pure acetone and then ultrasonically in deionized water for 10 min. The cleaned samples were dipped in mixing acid (HNO_3 and HF) aqueous solution at 60 °C for 20 h, boiled in 1.2 M NaOH aqueous solution for 5 h, and washed with deionized water before and after the alkali treatment. After the NaOH treatment, the samples were soaked in saturated Na_2HPO_4 solution at 40 °C for 15 h and then in saturated $Ca(OH)_2$ solution at 25 °C for 10 h for precalcification. The calcium phosphate (Ca–P) layers were prepared by immersing the pre-calcified samples in the simulated body fluid (SBF) with pH (7.4) and ion concentrations: $[Na^+] = 142.0$ mM, $[Cl^-] = 125.0$ mM, $[HCO_3{}^{2-}] = 27.0$ mM, $[K^+] = 5.0$ mM, $[Mg^{2+}] = 1.5$ mM, $[Ca^{2+}] = 2.5$ mM, $[HPO_4{}^{2-}] = 1.0$ mM, and $[SO_4{}^{2-}] = 0.5$ mM. After soaking in SBF for 3, 5 and 7 days, the samples were taken out, respectively, and rinsed with deionized water and then dried in an oven at 40 °C. The surfaces of the specimens were examined by environment scanning electron microscopy (ESEM, XL30), XRD and X-ray photoemission spectroscopy (XPS, PHL1600ESCA system).

3. Results

Fig. 2 shows the surface morphology of $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ bulk glassy alloys subjected to treatments of mixed acid

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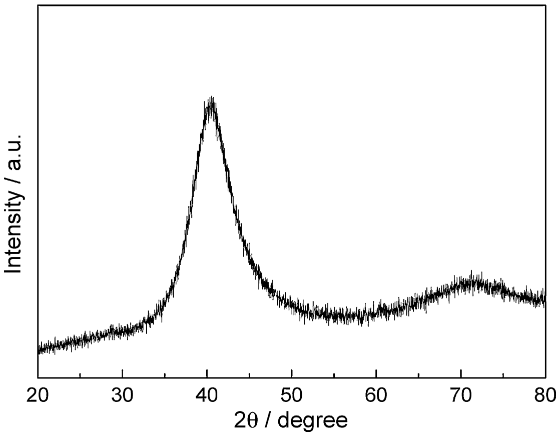

Fig. 1. XRD pattern of $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ bulk glassy alloy with diameter of 5 mm.

([HF] = 1.05 M, [HNO_3] = 1.55 M), subsequently 1.2 M NaOH solution, precalcification, and soaking in SBF for 3 day, 5 days, and 7 days, respectively. Numerous floccules appear on the sample surface after soaking 3 days (Fig. 2a). With increasing soaking time, floccules increase and form granules gradually (Fig. 2b). After 7 days soaking in SBF solution, a Ca–P coating is formed, but not completely (Fig. 2c). Fig. 3 shows the surface morphology of $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ bulk glassy alloy subjected to treatment of lower concentration mixed acid ([HF] = 0.42 M, [HNO_3] = 0.62 M), subsequently 1.2 M NaOH solution, precalcification, and soaking in SBF for 7 days. It can be seen the sample is completely covered by apatite coating consisted of lots of spherical particles.

Fig. 4 shows the XRD patterns of $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ bulk glassy alloy samples subjected to various chemical treatments. For the samples treated at higher acid concentration, deposition of Ca–P compounds is not significant. Only the sample soaked for 7 days exhibits some weak peaks which were identified as HA, such as Fig. 4(c). For the samples soaked for 3 or 5 days, the XRD patterns are consist of only broad diffraction halos which come from the bulk glassy alloy substrate, such as Fig. 4(a) and (b). This indicates that the amount of Ca–P depositions on the bulk glassy alloy were too low to detect by XRD measurement. However, for the sample treated at lower acid concentration, peaks of HA and $Ca_2P_2O_7$ are distinct and the glassy broad diffraction halo become very weak.

The sample subjected to lower acid-treated and immersion in SBF for 7 days was investigated by XPS. The corresponding XPS spectra are shown in Fig. 5. The XPS spectra over wild binding energy region exhibit peaks of carbon, oxygen, calcium and phosphorus. As we know, the C 1s peaks originate from the so-called contaminant carbon on the top of surface of samples. Ca 2p electron peaks exhibit an expected doublet feature at 346.9 and 350.8 eV, which correspond to a divalent oxidation state (Ca^{2+}) in inorganic calcium oxygen compound. P 2p peak exhibits a single peak at 133.6 eV, correspond to penta-valent (P^{5+}) oxidation state. Hence, the apatite coating is formed by combining the OH^-, $PO_4{}^{3-}$ and Ca^{2+} ions in SBF solution. No substrate element, such as Ti, Zr, Cu and Pd, was detected in the XPS spectra, indicating the complete coating with certain thickness over the depth which XPS could detect. In addition, the Ca/P atomic ratio of surface layer is 1.42 which is lower than that of pure HA(1.67), indicating that the Ca/P layer is composes of not only HA but also other Ca–P compound, such as $Ca_2P_2O_7$. This result is in accord with XRD results.

4. Discussion

Apatite has a better biocompatibility as compared with metallic implants and is grouped with the bioactive materials. Consequently, bioactive surface modification is in general applied to metallic materials for biomedical applications for the purpose of further improving their biocompatibility [17]. In applications of implants as bone plates for internal fixation, one key requirement for successful osseointegration, that is, bone bioactivity, is determined by the apatite-forming ability of the implant surface in body fluids. In vitro evaluation of apatite-forming ability is commonly carried out using immersion tests in a simulated body fluid (for example, Kokubo's SBF) for a soaking period of the order of a few

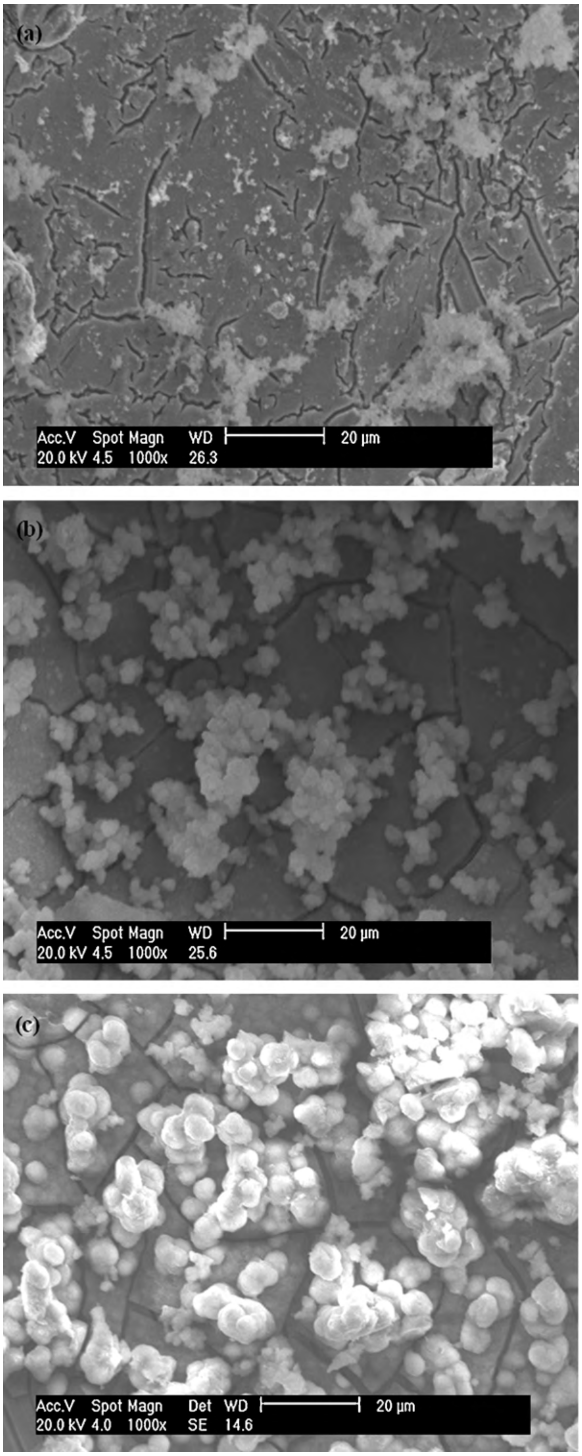

Fig. 2. Morphology of $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ bulk glassy alloys subjected to treatments of higher concentration mixed acid ([HF] = 1.05 M, [HNO_3] = 1.55 M) and soaking in SBF for 3 days (a), 5 days (b), and 7 days (c).

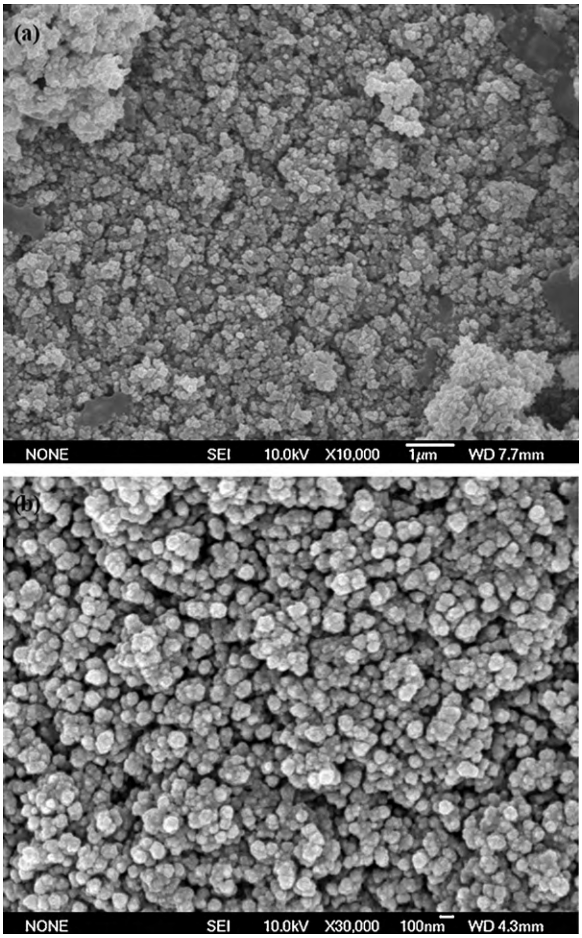

Fig. 3. Morphology of $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ bulk glassy alloy subjected to treatment of lower concentration mixed acid ([HF] = 0.42 M, [HNO_3] = 0.62 M) and soaking in SBF for 7 days.

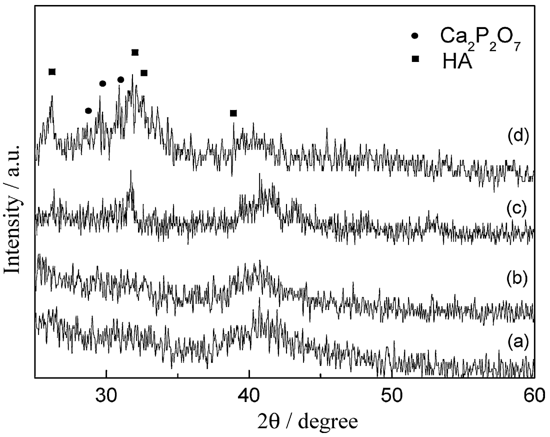

Fig. 4. XRD patterns of $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ bulk glassy alloy samples subjected to chemical treatments: dipping in higher concentration mixed acid ([HF] = 1.05 M, [HNO_3] = 1.55 M) and soaking in SBF for 3 day (a), 5 days (b), and 7 days (c) and dipping in lower concentration mixed acid ([HF] = 0.42 M, [HNO_3] = 0.62 M) and soaking in SBF for 7 days (d).

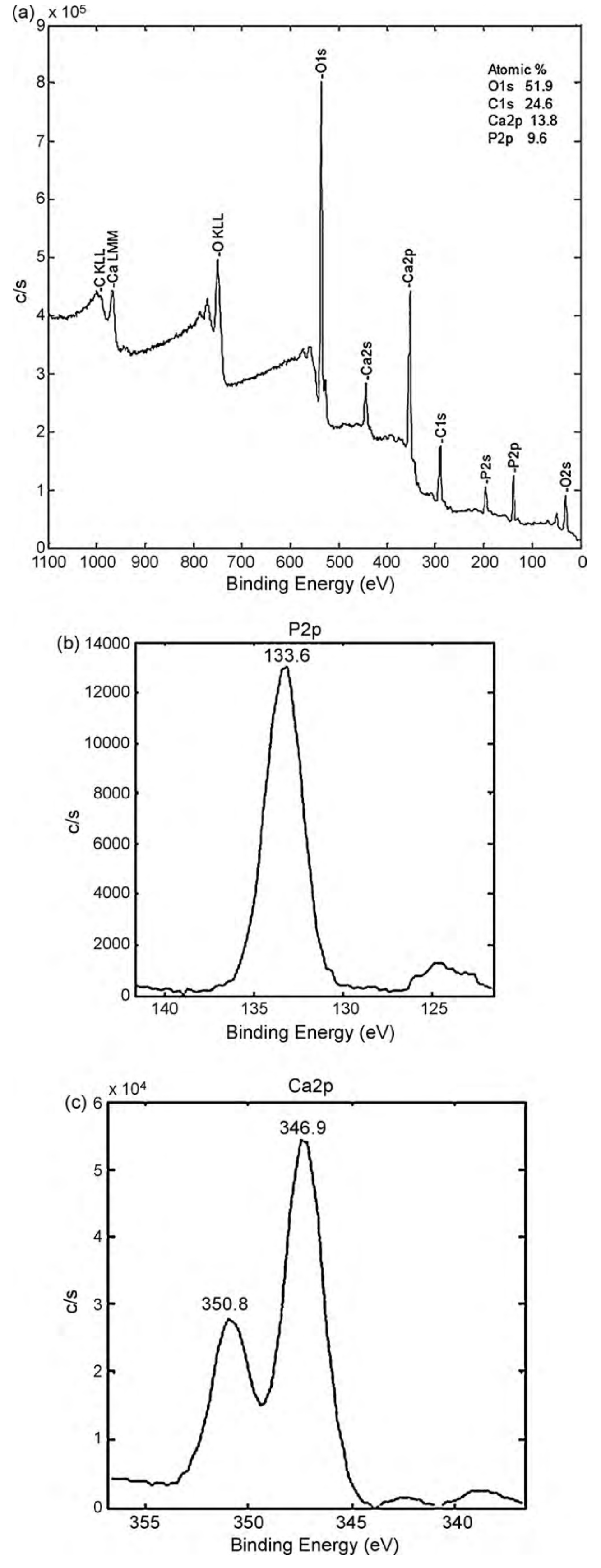

Fig. 5. XPS spectra of $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ bulk glassy alloy samples subjected to chemical treatments: dipping in lower concentration mixed acid ([HF] = 0.42 M, [HNO_3] = 0.62 M) and soaking in SBF for 7 days: XPS survey spectra (a), P 2p (b), and Ca 2p (c).

Table 1
Surface elements concentration.

	Elements				
	Ti	Zr	Cu	Pd	Sn
Blank sample (nominal) (at.%)	40	10	34	14	2
Acid-treated sample (at.%)	46.1	15.3	16.5	21.5	0.6

weeks [18,19], which are regarded as precursor tests for bone bioactivity. Extensive studies had been conducted on the treatment of alkali-treated Ti and Ti alloys soaked in SBF over the last decade, however, little paper reported the formation of apatite coating on the Ti-based bulk glassy alloys with lower Ti content.

The main arguments about apatite formation continue as to the mechanism of apatite formation on titanium [20]. As the main components of the TiZrCuPdSn alloy, Ti and Cu play important roles on the surface characters. The surface of TiZrCuPdSn bulk glassy alloy suffered selective corrosion when it was dipped in the mixed acid solution. Table 1 shows the surface concentration of $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ bulk glassy alloy sample subjected lower concentration mixed acid treatment. The concentration data were calculated from XPS results, in which the O and C were eliminated. The results show that the surface Cu content decrease to 16.5 at.%. However, Ti and Zr contents increase to 46.1 and 15.3 at.%, respectively. Although Cu is a kind of trace element which is necessary for human body, over release of Cu ion would hurt the body health. Hence, the decrease of Cu on surface is favor to cure safety. According the basic chemical character, active species of Cu on the TiZrCuPdSn alloy surface were dissolved first and inert species of Ti were oxidized according to the following reaction:

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO\uparrow + 4H_2O$$

$$3Ti + 4HNO_3 \rightarrow 3TiO_2{\cdot}2H_2O + 4NO\uparrow$$

According to this, a passive titanium oxide layer has formed on the surface of sample treated by the mixed acid mainly composed of HNO_3. Another effect of dipping in the mixed acid solution is preparing topological structure on the alloy surface. The topological surface is favor of not only formation of Ca–P coating, but also improving osseointegration of implant materials. Titanium oxide and zirconium oxide would be etched in the mixture acid with F^-. Chen et al suggested that acid immersion was advantageous for increasing the surface area for NiTi alloy by producing many pits or grooves [21]. However, high concentration F^- would result in over etching of Ti, furthermore decrease the content of Ti on the surface. Since formation of Ca–P coating on the surface is mainly owing to the Ti on the surface, higher F^- concentration would result in a lower apatite-forming ability.

Titanium can form $HTiO_3{}^-{\cdot}nH_2O$ when it is exposed to NaOH aqueous solution [21]. This negatively charged hydrate titanate reacts with positively Na^+ ions to form sodium titanate in order to maintain electrical neutrality. The same react should occur on the surface of Ti-based glassy alloy subjected to acid etching and then NaOH solution immersion. When the sodium tianate layer was soaking in SBF solution, Na^+ would be exchanged by H_3O^+ ions [21]. Thereby, the surface film of titania hydrogel $TiO_2{\cdot}nH_2O$ would formed and local pH of SBF near the layer surface would increase [22]. Kokubo et al. [23,24] reported that the prerequisite for apatite formation on biomaterials in the living body was the emergence of a type of functional group, such as Ti–OH groups, which could be an effective site for apatite nucleation on the materials surface in the human body fluid. The promoted precipitation of HA has been attributed to the increased number of nucleation sites and to the elevated supersaturation with respect to HA due to the pH increase. The formation of the Ca–P layer on metallic materials would improve the bioactivity and depress the harmful metallic ions release to human body.

5. Conclusions

A biomimetic apatite coating was successfully achieved on the $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ bulk glassy alloy by chemical surface treatment. By immersing acid–alkali-treated $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ bulk glassy alloy samples in saturated Na_2HPO_4 solution and then in saturated $Ca(OH)_2$ solution for precalcification, the bioactivity of the alloy surface was significantly improved. A dense and uniform calcium phosphate layer composed mainly of HA and $Ca_2P_2O_7$ was rapidly deposited on the pre-calcified $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ bulk glassy alloy in SBF within 7 days. Higher F^- concentration in the mixed acid would result in a lower apatite-forming ability.

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