分科会：生体・医療材料開発分野

生体適合高性能 Ti 基金属ガラス合金の改善と評価

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Improvement and characterization of biocompatible Ti-based metallic glasses

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1. Research Object

Ti-based bulk metallic glasses (BMGs) are promising materials for functional applications such as biomedical materials due to their high corrosion resistance, excellent mechanical properties and good biocompatibility. Many Ti-based BMGs have been developed in the framework of the Ti-Ni-Cu and Ti-Zr-Cu-Ni alloy systems. However, these Ti-based BMGs contain Ni and/or Be, etc., which are not suitable to be in contact with human body because of the cellar toxicity, limiting the application of Ti-based BMGs in medical fields. Recently, we developed Ni- and Be-free Ti-Zr-Cu-Pd BMGs with high strength and good corrosion resistance make it possible to create novel Ti-based BMG implants. However, relative low glass-forming ability (GFA) (with critical diameter of 7 mm) restricted the biomedical applications. In order to make better use in field of biomaterials, the Ti-Zr-Cu-Pd bulk glassy alloys need to modify for enhancing its glass-forming ability, machinability, thermal stability and mechanical properties.

Here, we report our recent progress about improvement of the Ti-Zr-Cu-Pd bulk glassy alloys.

2. Results and Discussion

2.1. Improvement of the Ti-Zr-Cu-Pd bulk glassy alloys

The minor addition is fundamental to controlling the formation, manufacture and properties of metallic materials by controlling nucleation during solidification. We investigated the effects of minor addition elements (Sn, Al, Si, Au, Ag, Pt, Fe, Cr, Nb and Ta) on the glass-forming ability (GFA), thermal stability, mechanical properties and corrosion behavior of the Ti-Zr-Cu-Pd bulk glassy alloy system. The results are summarized in Fig. 1.

The substitution of Cu by 2% Sn improved significantly the GFA. The $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ bulk glassy alloy rod with a diameter of 12 mm has been fabricated by copper mold casting technique. The addition of 2~4% Sn enlarged the supercooled liquid region, indicating good thermal stability. TiZrCuPdSn bulk glassy alloys exhibited high compressive strength of about 2000-2050 MPa. The minor additions of the Fe, Au, Ag, Pt, Nb and Ta improved the plasticity and corrosion behavior. While minor additions of Si, Ag, Fe, and Cr lowered the glass-forming ability, and Al and Cr additions were harmful to plasticity of the Ti-Zr-Cu-Pd glassy alloys.

High strength and distinct plastic strain were observed in the stress-strain curves for Nb-added Ti-Zr-Cu-Pd alloys. Especially, yield strength exceeding 2050 MPa, low Young's modulus of about 80 GPa and distinct plastic strain of 6.5 % and 8.5 % corresponding to serrated flow sections were obtained in the 1 % and 3 % Nb-added Ti-Zr-Cu-Pd alloys, respectively. The minor additions of noble metal elements (Au, Pt) improved significantly plastic stain of the Ti-Zr-Cu-Pd glassy alloys. The high resolution transmission electron microscopy observations demonstrated that there were nano-particles dispersed in the glassy matrix. Therefore, it was proposed that the distinct plastic strains should originate from the obstacle of nano-particles in glassy matrix to shear mode deformation.

Elements	Sn	Al	Si	Au	Ag	Pt	Fe	Cr	Nb	Ta
GFA	⇧	⇩	⇩	⇩	⇩	⇩	⇩	⇩	⇩	⇩
Plasticity	⇧	⇧	⇩	⇧	⇧	⇧	⇧	⇩	⇧	⇧
Corrosion resistance	⇧	−	−	⇧	⇧	⇧	⇧	⇧	⇧	⇧

Fig. 1 Effects of minor addition elements on the properties of the Ti-Zr-Cu-Pd bulk glassy alloy system.

In vivo evaluation of the biocompatibility has also been carried out by implantation the Ti-based ($Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$) glassy alloy bars under the skin and in the bone of rats. The Ti-based BMG bars exhibited excellent biocompatibility in both soft tissue and hard tissue, it also showed nice osteoconductivity when implanted in bone tissue and no metal ion diffusion was found up to three months after operation.

2.2. Ti-based bulk metallic glasses with high strength and large size

It is known that the BMGs are commonly produced using solidification techniques such as copper mold casting, water quenching, etc. However, using solidification technique, a rather high cooling rate is required to suppress the formation of more thermodynamically stable crystalline phases. Sample size and shape are seriously limited, thereby limiting the range of their applications. On the other hand, using consolidation technique, it is possible to produce larger metallic glassy alloy parts in a variety of shapes than those fabricated by solidification technique. Spark plasma sintering (SPS) process, as a developed rapid consolidation technique, has a great potential for producing large-size glassy samples in a short sintering time.

We prepared Ti-based metallic glassy powders using a high pressure argon gas atomization method. Using the glassy alloy powders, or their mixed powders blended with hydroxyapatite (HA) powder, we produced the Ti-based BMGs and the composites with a diameter over 15 mm by the SPS process. The samples sintered by the SPS process at a sintering temperature of 643 K with a loading pressure of 600 MPa exhibited high strength of 2060 MPa with high densification and a full glassy structure. Electrochemical measurements of the sintered samples were conducted in a three-electrode cell using a platinum counter electrode and a saturated calomel reference electrode (SCE). Potentiodynamic polarization curves were measured with a potential sweep rate of 0.83×10^{-3} V s^{-1} in Hanks' solution after immersing the samples for 420 s. The curve for the sample prepared at 643 K exhibited a flat passive region after active dissolution at open-circuit potential, having a higher pitting potential. For Ti-based glassy composite samples, the HA particles were in a polyhedral shape, and uniformly distributed in the whole sintered samples. No crystallization of the glassy matrix was observed. The thermal stability was almost independent of the addition of the HA particles. Significant deformation of Ti-based glassy powders was also observed. This is due to the viscous flow which can occur at the sintering temperature. With increasing the HA content to over 3 wt.%, distribution of the HA particles became inhomogeneous and partial crystallization was induced. The strength decreased with increase of the HA content. The sintered composites exhibited lower Young's moduli than those of the as-cast Ti-based glassy alloys. The Ti-based BMGs and the composites with excellent properties, satisfying dimension and without toxic elements make it possible to apply as biomedical materials.

Furthermore, we also produced porous Ti-based BMGs with the diameter over 15 mm by spark plasma sintered the mixture of the gas-atomized Ti-based glassy alloy powders and solid salt (NaCl) powders, followed by leaching treatment into water to eliminate the salt phase. The pores were homogeneously distributed in the whole sintered samples. The porosity can be controlled by controlling the volume fraction of the adding salt phase. The high strength porous Ti-based BMGs with low Young's modulus, which was approximate to that of natural bone, were obtained.

3. 論文発表

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