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Effects of Si addition on the glass-forming ability, glass transition and crystallization behaviors of $Ti_{40}Zr_{10}Cu_{36}Pd_{14}$ bulk glassy alloy

S.L. Zhu [a,*], X.M. Wang [a], F.X. Qin [a], M. Yoshimura [b], A. Inoue [a]

[a] Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
[b] Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan

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Abstract

The effects of small amounts of Si on the glass-forming ability, glass transition and crystallization behaviors of a $Ti_{40}Zr_{10}Cu_{36}Pd_{14}$ bulk glassy alloy were investigated. The addition of Si caused the decrease of glass-forming ability and the increase of the supercooled liquid region. The fragility of the alloys containing Si was higher than that of the Si-free alloy. In the glass transition process, both generation and annihilation of free volumes are suppressed by the addition of 1–3 at% Si. The activation energy for crystallization increases with increasing Si content, indicating the improvement of thermal stability. The crystallization structure of the alloys containing Si contents less than 4% consisted of six phases of $CuTi_2$, Ti, Cu_8Zr_3, Cu_4Ti_3, TiZr and $PdTi_2$.

Keywords: B. Glasses, metallic; B. Thermal stability; C. Rapid solidification processing; F. Calorimetry; F. Diffraction

1. Introduction

Bulk glassy alloys exhibit high mechanical strength and good corrosion resistance which enable us to use as structural and functional materials [1–4]. Since bulk glassy alloys were discovered in the late 1980s [1], a number of bulk glassy alloy systems, such as Mg-, La-, Zr-, Pd-, Ti-, Fe-, Co-, Ni- and Cu-based systems, have been developed [5]. Ti-based bulk glassy alloys are expected to be applied as biomaterials because of their excellent corrosion resistance, good biocompatibility, low Young's modulus and high recovery of strain (>2%). Some works have been made on Ti-based bulk glassy alloys, such as Ti–Ni–Cu [6], Ti–Ni–Cu–Co [7], Ti–Cu–Ni–Sn [8], Ti–Zr–Cu–Ni [9] and other Ti–Be-based [10] systems. But the toxic elements, such as Ni, Al and Be, in their alloys are dangerous for applications to biomaterials. Recently, we have developed a new Ti–Zr–Cu–Pd bulk glassy alloy without toxic elements, which has high potential of biomedical applications. The Ti–Zr–Cu–Pd alloy was cast into glassy alloy rods with critical diameters up to 6 mm, indicating its high glass-forming ability (GFA). The Ti-based bulk glassy alloy has higher strength and lower Young's modulus than those of conventional biomedical Ti alloys and seems to be favorable for future application as biomaterials [11].

On the other hand, the alloys with a high GFA often show a large supercooled liquid (SCL) region, ΔT_x, which is defined by the temperature range between glass transition temperature T_g and onset temperature of crystallization T_x. A large SCL region indicates high thermal stability of the glassy alloy and is in favor of secondary working by viscous flow deformation. Some previous papers have reported the influence of Si on the GFA and thermal stability of Ti–Zr–Hf–Cu–Ni–Si [12], Ti–Zr–Cu–Ni–Si [13] and Ti–Ni–Cu–B–Sn–Si [14] bulk glassy alloys. In the present paper, we explore the effect of Si on the GFA, glass transition and crystallization behaviors of the Ti–Zr–Cu–Pd bulk glassy alloy.

2. Experimental procedure

Ingots of a series of alloys with composition of $(Ti_{0.4}Zr_{0.1}Cu_{0.36}Pd_{0.14})_{100-x}Si_x$ were prepared by arc-melting the mixtures

* Corresponding author. Tel.: +81 22 215 2718; fax: +81 22 215 2381.
E-mail address: slzhu@imr.tohoku.ac.jp (S.L. Zhu).

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consisting of pure elements with purities above 99.9% in an argon atmosphere. The alloy composition represents nominal atomic percentage of the mixture. The ribbons and cylindrical rods with different diameters were prepared by melt spinning and copper mold casting, respectively. Glassy structure and crystallization phases were examined by X-ray diffraction (XRD). Thermal parameters were examined by differential scanning calorimetry (DSC) and differential thermal analysis (DTA).

3. Results and discussion

Fig. 1 shows the DSC curves of melt-spun $(Ti_{0.4}Zr_{0.1}Cu_{0.36}Pd_{0.14})_{100-x}Si_x$ ($x = 0$, 1, 2, 3, 4, 5) alloy ribbons measured at a heating rate of 0.67 K/s. It is found that these alloys exhibit two or three exothermic events due to a multi-stage crystallization depending on Si content. Moreover, the distinct glass transition is observed in the temperature range before crystallization for all the alloys. Fig. 2 shows the DTA curves obtained during continuous heating at a heating rate of 0.33 K/s for various alloy ingots. The glass transition temperature (T_g or $T_{g\text{-onset}}$), onset temperature of crystallization (T_x), onset temperature of melting (T_m), liquidus temperature (T_l) and other thermodynamic parameters are summarized in Table 1. The T_g, T_x and T_l shift to a higher temperature side with increasing Si content. The T_m also increases slightly with increasing Si content. The reduced glass transition temperature (T_{rg}) defined by the ratio of T_g to T_l has been successfully used to evaluate the GFA of various glassy alloys. The highest value of T_{rg} is obtained for $x = 0$ ($Ti_{40}Zr_{10}Cu_{36}Pd_{14}$ alloy) (shown in Table 1). With increasing Si content, the T_{rg} decreases, indicating the decrease of GFA. The largest supercooled liquid (SCL) region of 75 K is obtained for the $(Ti_{0.4}Zr_{0.1}Cu_{0.36}Pd_{0.14})_{97}Si_3$ glassy alloy, indicating the highest thermal stability. Some papers reported that the addition of a small amount of Si was effective for the increase in GFA of alloys [13,15,16]. However, the addition of Si for the $Ti_{40}Zr_{10}Cu_{36}Pd_{14}$ alloy would degrade the GFA substantially. The critical diameters (D_{max}s) are listed in Table 1. Some possibility for the decrease of GFA should be considered. With the addition of Si, the liquidus temperature (T_l) increases significantly and T_{rg} decreases. The melting temperature interval $T_l - T_m$ increases by Si addition, indicating the increase in the degree of the deviation from eutectic composition.

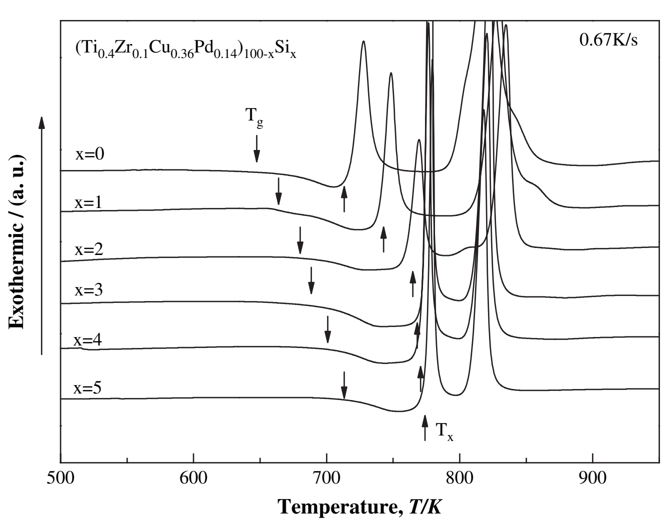

Fig. 1. DSC curves of $(Ti_{0.4}Zr_{0.1}Cu_{0.36}Pd_{0.14})_{100-x}Si_x$ ($x = 0$, 1, 2, 3, 4, 5) glassy alloys.

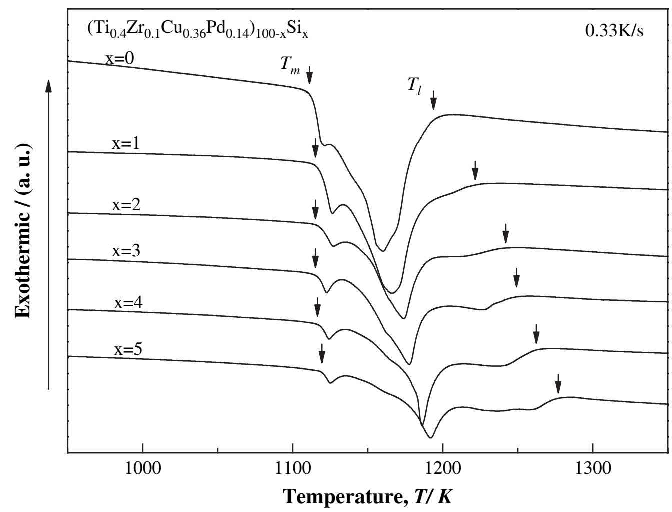

Fig. 2. DTA curves of $(Ti_{0.4}Zr_{0.1}Cu_{0.36}Pd_{0.14})_{100-x}Si_x$ ($x = 0$, 1, 2, 3, 4, 5) alloys.

The heating rate dependence of characteristic temperatures reflects the kinetic mechanisms of the structural relaxation and the phase transformation in the glasses or supercooled liquids. These processes can determine the fragility of supercooled liquid, which reflects the sensitivity of the liquid structure to temperature changes, because the viscosity relaxation and the glass transition measured by calorimetric methods occur on the same timescale [17]. The minor amount of Si may facilitate the formation of a new local atomic structure. The change of local atomic structure would influence the GFA of alloys significantly. It is found that there exists a correlation between short-range ordering and fragility, e.g., the stronger tendency of short-range ordering in stronger glass former [18]. In the present paper, the dynamic fragility parameter m was obtained by the Vogel–Fulcher–Tamman (VFT) method [19,20]. The dependence of T_g on heating rate β can be evaluated by following VFT formula:

Table 1
Thermal parameters of $(Ti_{0.4}Zr_{0.1}Cu_{0.36}Pd_{0.14})_{100-x}Si_x$ ($x = 0$, 1, 2, 3, 4, 5) glassy alloys

x	T_g/K	T_x/K	T_m/K	T_l/K	T_{rg}	D_{max}/mm	E_p/(kJ/mol)
0	669	718	1114	1191	0.562	6	287.6
1	680	740	1116	1220	0.557	4	289.5
2	691	759	1116	1242	0.556	4	304.1
3	695	770	1116	1250	0.556	3	311.0
4	704	773	1117	1264	0.555	2	327.7
5	713	774	1118	1284	0.555	<2	343.0