Thermal Stability and Mechanical Properties of Ti_{47.4}Cu_{42}Zr_{5.3}TM_{5.3} (TM = Co, Fe) Metallic Glass Sheets Prepared by Twin-Roller Casting Method

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Since Ti-based glassy alloys have high strength and high corrosion resistance, it is useful for an application field of substitution material for biomaterials such as living body bone. For the biomaterial use, the glassy alloys are required to substitute the harmful elements for the human body such as Ni. In the present study, we prepared the Ti_{47.4}Cu_{42}Zr_{5.3}TM_{5.3} (TM = Co, Fe) glassy alloy sheets by a twin-roller casting method, and investigated their thermal stability and mechanical properties. The prepared alloy sheets had flat surfaces with highly white luster, and exhibited a distinct glass transition typical to a glassy phase. The super-cooled liquid region \( \Delta T_f \) defined by the difference between the glass transition temperature \( T_g \) and the onset temperature for crystallization \( T_X \) is 50 K for the Ni-containing alloy, 36 K for the Co-containing alloy and 32 K for the Fe-containing alloy. All the alloy sheets exhibit good bending ductility and their Vickers hardness is in the range of 590 to 600.

1. Introduction

It is known that Ti-based glassy alloys have high strength, high hardness, high fracture toughness, high fatigue resistance, high corrosion resistance, and so on,\(^{1,2,4}\) and hence are expected to be applied to substitute materials as a living body bone. However, most of Ti-based glassy alloys, which have high glass-forming ability, include Ni element. Ni element has been thought to cause an allergic reaction\(^{5}\) in weak acidic medium like the living body, although the ease of the reaction is dependent on each person. If we choose the use of a glassy alloy as the alternative material of the living body bone, the glassy alloy material must consist of harmless and insoluble elements to the human body. Although some Ni-less Pd-containing glassy alloys have high glass-forming ability,\(^6\) the alloy has a disadvantage of high price and Pd is not greatly effective for resistance of allergic reaction.

Recently, we have investigated thermal stability and annealing-induced embrittlement behavior of Ti_{47.4}Cu_{42}Zr_{5.3}Ni_{15.3} glassy alloy sheet produced by a twin-roller casting method.\(^7\) The glassy alloy has a large supercooled liquid region, and shows good ductile-brittle behavior. That is, the degree of ductility changes gradually on heat treatment. Since Co and Fe are similar to Ni, we chose them as the substitute elements in the glassy alloy. In the present study, we aim to investigate the thermal stability and mechanical properties of the Ti_{47.4}Cu_{42}Zr_{5.3}TM_{5.3} (TM = Ni, Co, Fe) glassy alloys.

2. Experimental Procedure

The Ti_{47.4}Cu_{42}Zr_{5.3}TM_{5.3} (TM = Ni, Co, Fe) glassy alloys (composition given as nominal at%) were produced by a twin-roller casting method. The ingots were prepared by arc-melting in an Ar atmosphere.\(^7\) Phase identification and thermal analysis were performed by X-ray diffractometer (XRD) with Cu-K\(\alpha\) radiation and differential scanning calorimetry (DSC) with a constant heating rate of 0.67 Ks\(^{-1}\), respectively.

Tensile fracture strength of sheet samples was measured at room temperature in air by using an Instron-type tensile testing machine at a strain rate of 7.8 \times 10^{-4} \text{s}^{-1}. The tensile samples were prepared by wire-cutting of the glassy alloy sheets with the gauge length of 17 mm and thickness of 0.15 to 0.20 mm.

The ductile-brittle behavior after isothermal annealing was tested for the glassy alloy sheet samples annealed for 172.8 ks at different temperatures of 500, 550, 600 and 650 K, respectively. The samples were annealed in a vacuumed silica capsule. Hardness (HV) measurements were carried out by a Vickers micro-hardness tester with a 0.1 N force for 10 s. An average value of 6 measurement points was calculated. On the other hand, the degree of ductility was determined by a bend fracture test\(^{8-10}\) using the fracture strain \( \varepsilon_f = (s_f - s)/s \), where \( s_f \) is the distance between the both ends of the samples at fracture and \( s \) is the thickness of the sheet sample.

3. Results and Discussion

3.1 Phase identification and thermal properties

Table 1 The glass transition and crystallization temperatures and their mechanical properties of Ti_{47.4}Cu_{42}Zr_{5.3}TM_{5.3} (TM = Ni, Co, Fe) alloy sheets.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>( T_g ) [K]</th>
<th>( T_X ) [K]</th>
<th>( \Delta T_f ) [MPa]</th>
<th>( \sigma_f)-comp [MPa]</th>
<th>( \sigma_f)-tens [MPa]</th>
<th>HV [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti_{47.4}Cu_{42}Zr_{5.3}Ni_{15.3} (Ref)</td>
<td>690</td>
<td>90</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Ti_{47.4}Cu_{42}Zr_{5.3}Co_{15.3} (Ref)</td>
<td>673</td>
<td>715</td>
<td>43</td>
<td>1926</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Ti_{47.4}Cu_{42}Zr_{5.3}Fe_{15.3} (Ref)</td>
<td>638</td>
<td>688</td>
<td>50</td>
<td>1496</td>
<td>550</td>
<td>---</td>
</tr>
<tr>
<td>Ti_{47.4}Cu_{42}Zr_{5.3}Ni_{15.3}</td>
<td>658</td>
<td>694</td>
<td>36</td>
<td>1421</td>
<td>590</td>
<td>---</td>
</tr>
<tr>
<td>Ti_{47.4}Cu_{42}Zr_{5.3}Co_{15.3}</td>
<td>655</td>
<td>687</td>
<td>32</td>
<td>1377</td>
<td>600</td>
<td>---</td>
</tr>
</tbody>
</table>

Figure 1 shows the outer shape of the Ti_{47.4}Cu_{42}Zr_{5.3}TM_{5.3} (TM = Co, Fe) alloy sheets of about 17 to 19 mm in width and 0.15 to 0.21 mm in thickness prepared by the twin-roller casting method. The alloy sheets have very flat surfaces with highly white luster, and no contrast corresponding to the
precipitation of a crystalline phase is seen. Figure 2 shows the XRD profiles of the Ti_{47}Cu_{42}Zr_{5}\_TM_{5}\_3(TM = Ni, Co, Fe) alloy sheets in an as-prepared state, which consist only of halo peaks typical for a glassy structure. Figure 3 shows the DSC profiles. The glassy alloy shows characteristic endothermic-heat flow at the glass transition temperature. The Ti_{47}Cu_{42}Zr_{5}\_Ni_{5}\_3 alloy shows a distinct endothermic peak due to the glass transition at 638 K, followed by an exothermic peak due to crystallization at 688 K. Thus, the T_g, T_x and ΔT_x values are 638, 688 and 50 K, respectively. The T_g, T_x and ΔT_x values for Ti_{47}Cu_{42}Zr_{5}\_Co_{5}\_3 and Ti_{47}Cu_{42}Zr_{5}\_Fe_{5}\_3 glasses are 655, 687 and 32 K, respectively. For Ti_{47}Cu_{42}Zr_{5}\_TM_{5}\_3(TM = Ni, Co, Fe) glassy alloys, 3.2 Mechanical properties

Figure 4 shows the relative values of tensile fracture strength for the Ti_{47}Cu_{42}Zr_{5}\_TM_{5}\_3(TM = Ni, Co, Fe) glassy alloy sheets, based on the tensile fracture strength of the Zr_{55}Al_{10}Ni_{5}Cu_{30} glassy alloy.\textsuperscript{8,11} The relative tensile strength of the Ti_{47}Cu_{42}Zr_{5}\_TM_{5}\_3(TM = Ni, Co, Fe) glassy alloy sheets shows 2 to 11% higher than that of the Zr_{55}Al_{10}Ni_{5}Cu_{30} glassy alloy sheet. Although the Ti_{47}Cu_{42}Zr_{5}\_Ni_{5}\_3 glassy alloy sheet shows the highest strength among the glassy alloys studied, the strength of the Ti_{47}Cu_{42}Zr_{5}\_Fe_{5}\_3 alloy differs by...
5 to 8%. Figure 5 shows the fracture surface of the Ti$_{47}$Cu$_{42}$Zr$_{5}$TM$_{3.3}$ (TM = Ni, Co, Fe) glassy alloy sheets after tensile fracture test, which exhibits a vein-like pattern typical for a glassy alloy. Figure 6 shows the annealing temperature dependence of Vickers micro-hardness for the Ti$_{47}$Cu$_{42}$Zr$_{5}$TM$_{3.3}$ (TM = Ni, Co, Fe) glassy alloy sheets. The hardness of the as-cast Ti$_{47}$Cu$_{42}$Zr$_{5}$TM$_{3.3}$ (TM = Ni, Co, Fe) glassy alloy sheets is 550 ± 5, 590 ± 5 and 600 ± 5, respectively. The hardness of Ti$_{47}$Cu$_{42}$Zr$_{5}$Ni$_{5}$ glassy alloy increased to 660 by annealing at 650 K. Similarly the Ti$_{47}$Cu$_{42}$Zr$_{5}$TM$_{3.3}$ (TM = Co and Fe) glassy alloys significantly increased to 690 by the annealing. The difference in the influence of the annealing temperature on hardness is considered to arise from the difference in the glass transition temperature, which reflects the thermal stability of the supercooled liquid of the glassy alloys as shown in Fig. 3. Figure 7 shows the change in the bending fracture strain with annealing temperature for the Ti$_{47}$Cu$_{42}$Zr$_{5}$TM$_{3.3}$ (TM = Ni, Co, Fe) glassy alloy sheets. The alloy sheets become brittle above 500 K and completely lose their ductility above 550 K ($\sigma_f = 0.03$ to 0.07), although the Ti$_{47}$Cu$_{42}$Zr$_{5}$Fe$_{5.3}$ glassy alloy embrittles less than other glassy alloys. Figure 8 shows the annealing time dependence of the diffraction angle (2 theta) of XRD for the Ti$_{47}$Cu$_{42}$Zr$_{5}$TM$_{3.3}$ (TM = Ni, Co, Fe) glassy alloys. The diffraction angle change means the change in interatomic mean-distance from
approximate calculation using length of X-ray radiation. The mean distance becomes shorter with increasing annealing temperature, accompanied with structural relaxation and decrease in the free-volume of the glassy alloys.\(^{12-14}\) The atomic radius, which is estimated from hard sphere model, is 0.125 nm for Ni, 0.125 nm for Co and 0.126 nm for Fe.\(^{15}\) Accordingly, the mean distance remains almost unchanged, \(i.e.,\) about 0.217 (\(2\theta = 40.7^\circ\)) to 0.218 nm (\(2\theta = 40.5^\circ\)) for the \(Ti_{47.4}Cu_{42}Zr_{5.3}TM_{5.3}\) (TM = Ni, Co, Fe) glassy alloys. In other words, since the structure of glassy alloys does not greatly change substituting Ni with Co or Fe, it is considered that the mechanical properties are not much sensitive to the alloying element. On the other hand, as shown in Fig. 3, the supercooled liquid region of the \(Ti_{47.4}Cu_{42}Zr_{5.3}TM_{5.3}\) (TM = Ni, Co, Fe) glassy alloys decreases from 50 to 33 K depending on the alloying element. This means that the thermal stability is affected greatly by the difference in the electronic state between Ni and Co or Fe.

4. Conclusions

We prepared the \(Ti_{47.4}Cu_{42}Zr_{5.3}TM_{5.3}\) (TM = Ni, Co, Fe) glassy alloy sheets using the twin-roller casting method, and investigated their thermal stability and mechanical properties. From the thermal analysis, the supercooled liquid region of the glassy alloys extends in the temperature interval of 50 K(TM = Ni), 36 K(TM = Co) and 32 K(TM = Fe). On the other hand, the tensile fracture strength is 1496 (TM = Ni), 1421 (TM = Co) and 1377 MPa (TM = Fe), and the hardness (Hv) is 550(TM = Ni), 590(TM = Co) and 600(TM = Fe).

The hardness and fracture strain at the initial state remain unchanged below 500 K, and there is no significant difference in the mechanical properties upon the substitution of the alloying elements from Ni to Co or Fe. The change in the thermal stability with substitution of the elements cannot be neglected. The substitution is effective for application as biomaterials because the change in the mechanical properties is also small.

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REFERENCES