Effect of alloy composition on phase transformation behavior of Zr-Cu shape memory alloy

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In the current study, we investigated the effect of alloy composition and heat treatment on the microstructure, thermal properties, and hardness of near-equiatomic Zr-Cu alloys. Zr-Cu alloys with near-equiatomic compositions were fabricated by an arc-melting method. Furthermore, some samples were heated at 800 °C for 1 hour in an electric furnace, and then quenched in water. The samples, both before and after quenching, were analyzed by X-ray diffraction (XRD), differential scanning calorimetry (DSC), and Vickers hardness testing. It was confirmed that the Zr-Cu alloys consisted of three intermetallic compounds, ZrCu, Zr₂Cu and Zr₇Cu₁₀. The volume fractions of these intermetallic compounds were affected by the alloy composition and quenching. Furthermore, it was confirmed that the fabricated Zr-Cu alloys exhibit martensitic and reverse martensitic transformation with cooling and heating processes, respectively. However, the martensitic and reverse martensitic transformation temperatures showed very little change with varying alloy composition and quenching. In contrast, it was found that the Vickers hardness does change with varying alloy composition and quenching.

Key words: shape memory alloy, martensitic transformation, alloy composition, quenching

1. INTRODUCTION

The equilibrium phase diagram of the Zr-Cu binary alloy suggests that, at room temperature, a Zr-Cu alloy with near-equiatomic alloy composition consists of the two intermetallic compounds Zr₂Cu and Zr₇Cu₁₀. The third intermetallic compound of B2-type ZrCu (P) exists at temperatures above 715 °C.^[1] ZrCu (P) experiences a martensitic transformation (MT) into ZrCu (M) with rapid cooling. The MT behavior of ZrCu is similar to that of Ti-Ni alloys, a typical shape memory alloy (SMA).^{[2][3]} Ti-Ni alloys have been studied extensively regarding shape-memory behaviors and the effects of influencing factors such as alloy composition, heat treatment, and surface treatment. Both MT and reverse MT temperatures for the Ti-Ni system are decreased by approximately 100 °C with an increase in Ni concentration of only 1 at.%. Despite this extensive research, commercial Ti-Ni SMA is limited to applications at temperatures below 100 °C, as the reverse MT temperature is below 100 °C.

It has been reported that the intermetallic compound ZrCu also exhibits shape-memory behavior, with considerable promise as high-temperature SMAs. The reverse MT temperature of Zr-Cu alloys ranges from 280 to 420 °C^[1]; therefore, the shape-memory behavior of Zr-Cu alloys may be applicable in many uses requiring high temperatures, such as applications in the automotive, aerospace, electrical, and architectural industries. However, very few studies have reported on the shape-memory behavior of Zr-Cu alloys.

The purpose of this study is to investigate the material properties of Zr-Cu alloys with near-equiatomic compositions. In this study, we focus on the microstructure, MT and reverse MT temperature, and

hardness. The effects of alloy composition on the microstructure and MT and reverse MT temperature of the Zr-Cu alloys are investigated. The shape-memory behaviors of Zr-Cu alloys fabricated by heat treatment are analyzed. In addition, the hardness of the Zr-Cu alloys is investigated.

2. EXPERIMENTAL PROCEDURES

2.1 Materials and specimen

Zr-Cu binary alloys of different compositions were fabricated. The composition of the materials could be expressed as Zr-*x*Cu, where *x* was the Cu concentration; *x* = 48, 49, 50, 51, and 52 at.%. The master alloy ingots were fabricated by arc-melting a mixture of highly purified Zr(99.99%) and Cu(99.99%) in an Ar atmosphere. The master alloy ingots were remelted several times in order to ensure chemical homogeneity. Thin plate-type specimens were prepared measuring 6 × 3 × 0.5 mm. Some specimens were used as-is; others were heated to 800 °C for 1 h in an electric furnace and then quenched in water. These specimens are abbreviated as “non-heat treated” and “quenched,” respectively.

2.2 Structural analysis and investigation of thermal properties and hardness

The microstructure of the specimens was analyzed at room-temperature (about 20°C) by X-ray diffraction (XRD) (Rigaku, UltimaIV) using Cu K_α radiation. Differential scanning calorimetry (DSC) (Shimadzu, DSC60) was performed in N₂ gas at heating and cooling rates of 0.167 °C/s. Furthermore, Vickers hardness

Fig.1 XRD patterns of non-heat treated Zr- x Cu alloys. (a) $x = 52$, (b) $x = 51$, (c) $x = 50$, (d) $x = 49$ and (e) $x = 48$ (at.%).

testing (Shimadzu, HMV2) was performed with an applied load of 4.9 N and holding time of 15 s.

3. RESULTS and DISCUSSION

3.1 Structural analysis

The effect of composition on the microstructure of near-equiatomic Zr-Cu alloys was investigated by XRD. Figure 1 shows the room-temperature XRD patterns of the non-heat-treated alloys with different compositions; the patterns show that the non-heat-treated Zr-Cu alloys contain the two equilibrium phases of Zr_2Cu and Zr_7Cu_{10} as well as the martensite $ZrCu$ (M) phase, regardless of composition. For Cu-rich alloys (Figs. 1 (a) and (b)), the number of Zr_7Cu_{10} peaks is increased. Meanwhile, for Zr-rich alloys (Figs. 1 (d) and (e)), the number of Zr_2Cu peaks is increased. These pattern changes confirm that the microstructures of near-equiatomic Zr-Cu alloys vary with changes in the composition.

As shown in Figs. 1 (d) and (e), the Zr-rich alloys possess an unidentified peak at about $2\theta = 57^\circ$. The peak corresponds to neither $ZrCu$ (M) nor the Zr_2Cu or Zr_7Cu_{10} equilibrium phases. At present, the origin of this peak is unknown. Further detailed study is necessary to resolve the microstructures of these alloys.

The effect of quenching on the microstructure of the near-equiatomic Zr-Cu alloys was investigated. Figure 2 shows the room-temperature XRD patterns of quenched Zr-Cu alloys of varied compositions. As shown, the number of peaks corresponding to Zr_2Cu and Zr_7Cu_{10} are obviously decreased, even in Zr-rich and Cu-rich alloys. Quenched Zr-50Cu alloy is found to consist of monolithic $ZrCu$ (M); both Zr_2Cu and Zr_7Cu_{10} phases disappear after quenching, as shown in Fig.2 (c). This demonstrates that the Zr-50Cu alloy consists of monolithic $ZrCu$ (P) after heating to 800 °C for 1 h; $ZrCu$ (P) fully transforms into $ZrCu$ (M) during rapid cooling. This indicates that quenching the Zr-Cu alloys restricts the decomposition of

Fig.2 XRD patterns of quenched Zr- x Cu alloys. (a) $x = 52$, (b) $x = 51$, (c) $x = 50$, (d) $x = 49$ and (e) $x = 48$ (at.%).

$ZrCu$ (P) into Zr_2Cu and/or Zr_7Cu_{10} , and enhances the MT of $ZrCu$ (P) to $ZrCu$ (M).

The microstructures of quenched Cu-rich alloys can be predicted by the equilibrium phase diagram. Cu-rich alloys consist of $ZrCu$ (P) and proeutectoid Zr_7Cu_{10} after heating to 800 °C for 1 h, because $ZrCu$ (P) is a line compound. After rapid cooling, $ZrCu$ (M) forms by the same mechanism as occurs in the Zr-50Cu alloy. Proeutectoid Zr_7Cu_{10} exhibits no phase transformation during rapid cooling. As a result, the quenched Cu-rich alloys consist of $ZrCu$ (M) and Zr_7Cu_{10} , as shown in Figs. 2 (a) and (b). Meanwhile, quenched Zr-rich alloys consist of $ZrCu$ (M), Zr_2Cu , and Zr_7Cu_{10} , as shown in Figs. 2 (d) and (e). The existence of Zr_7Cu_{10} suggests that both MT from $ZrCu$ (P) to $ZrCu$ (M) and a eutectoid transformation from $ZrCu$ (P) to Zr_2Cu and Zr_7Cu_{10} occur during quenching. These results imply that the cooling rate, obtained by water quenching, approached the critical cooling rate of $ZrCu$.

3.2 MT and reverse MT temperature

The phase transformation temperatures of both non-heat-treated and quenched Zr-Cu alloys of varying compositions were evaluated by DSC. Figure 3 shows an example of DSC measurement of the non-heat-treated Zr-50Cu alloy. As shown, endothermic and exothermic peaks are observed during the heating and cooling processes, respectively. Because the endothermic and exothermic peaks correspond to the reverse MT and MT, respectively, the start and finish temperatures of the reverse MT (A_s , A_f) and MT (M_s , M_f) can be evaluated. Similar endothermic and exothermic reactions are observed in the DSC results from both non-heat-treated and quenched Zr-Cu alloys of other compositions. The obtained A_s , A_f , M_s , and M_f are summarized in Fig. 4. Although the A_s and A_f of the quenched Zr-Cu alloys increase slightly with increases in the Zr concentration,

Fig.3 DSC patterns of non-heat treated Zr-50Cu alloy.
(a) Heating run and (b) Cooling run.

Fig.4 Relationship between MT (M_s and M_f) and reverse MT (A_s and A_f) temperatures and Cu concentration. Results of non-heat treated and quenched Zr-Cu alloys are plotted.

the A_s , A_f , M_s , and M_f of both non-heat-treated and quenched alloys remain nearly unchanged with changes in composition. For example, the A_f of non-heat-treated and quenched Zr-Cu alloys is about 310 °C for all five tested compositions. Therefore, A_s , A_f , M_s , and M_f temperatures for near-equiatomic Zr-Cu alloys are not significantly influenced by compositional variations, in contrast with the compositional dependence of these values in the Ti-Ni system.

3.3 Volume fraction of the martensitic phase

The possibility of controlling the microstructures of near-equiatomic Zr-Cu alloys was investigated. We focused on the ZrCu (M) volume fraction v_f in each Zr-Cu alloy. Based on the DSC methodology, the v_f of a specific crystalline phase was calculated as the ratio of the transformation enthalpy of the sample to a reference value. In this study, the relative volume fraction $v_f/v_{f(ref)}$ was calculated by the following equation:

$$\frac{v_f}{v_{f(ref)}} = \frac{\Delta H_{sam}}{\Delta H_{ref}} \quad (1)$$

where $v_{f(ref)}$ is the v_f value of ZrCu (M) in a reference material and ΔH_{ref} and ΔH_{sam} are the reverse MT enthalpies of the reference material and sample, respectively. We used the quenched Zr-50Cu alloy as the reference material. Figure 5 shows the $v_f/v_{f(ref)}$ values obtained from both non-heat-treated and quenched Zr-Cu alloys of varied compositions.

The $v_f/v_{f(ref)}$ values of the quenched alloys are higher than those of the non-heat-treated alloys for all compositions. The value for quenched Zr-50Cu alloy is about 13% higher than that for non-heat-treated Zr-50Cu alloy. The difference in these values results from the precipitation of Zr_2Cu and Zr_7Cu_{10} in the non-heat-treated Zr-50Cu specimen, as shown in Fig. 1(c).

In both quenched and non-heat-treated Zr-Cu, the $v_f/v_{f(ref)}$ value varies with composition. The $v_f/v_{f(ref)}$ value is the largest for the Zr-50Cu alloy and is decreased with increases in either Zr or Cu concentrations. The decreasing ratio of the $v_f/v_{f(ref)}$ value for the quenched alloys is smaller than that for the non-heat-treated alloys. Because this indicates larger volume fractions of ZrCu (M), quenching is concluded to be effective in inducing the MT of near-equiatomic Zr-Cu alloys.

3.4 Relationship between hardness and microstructure

The Vickers hardness of both non-heat-treated and quenched Zr-Cu alloys with different compositions were investigated. Figures 6 and 7 show the results of the

Fig.5 The volume fraction of ZrCu (M-phase) in both non-heat treated and quenched Zr-xCu alloys.

Fig.6 Relationship between Vickers hardness of the near-equiatomic Zr-Cu alloys and Zr concentration. Results of non-heat-treated Zr-Cu alloys

Vickers hardness tests; the error bars in Figs. 6 and 7 represent the maximum and minimum values achieved for each test condition.

For non-heat-treated alloys (Fig.6), the hardness depends on the composition. The equiatomic Zr-Cu alloy exhibits the minimum hardness value, and the hardness increases with increases in either Zr or Cu concentrations. For example, the average hardness of Zr-52Cu alloy is about 10% higher than that of the Zr-50Cu alloy. The higher hardness values for Zr- or Cu-rich Zr-Cu alloys can be understood by considering the precipitation of Zr_2Cu or Zr_7Cu_{10} within the specimen. In general, intermetallic compounds have mixed interatomic bonding, showing metallic, covalent, and ionic bonding types. Because of this strong interatomic bonding, intermetallic compounds exhibit higher hardness than solid solutions do. For non-heat-treated Zr-Cu alloys, XRD and DSC results reveal that the volume fractions of the intermetallic Zr_2Cu or Zr_7Cu_{10} phases increase with increases in Zr or Cu concentrations. These phases induce the hardening of the material, as shown in Fig. 6.

For the quenched alloys (Fig. 7), although the hardness of the quenched alloy depends on the composition, the rate of hardness change with changes in composition is smaller than that in the non-heat-treated alloy. For example, the average hardness of the quenched Zr-52Cu alloy is only 5% higher than that of the quenched Zr-50Cu alloy. As quenching restricts the decomposition of ZrCu (P) to Zr_2Cu or Zr_7Cu_{10} , the volume fractions of Zr_2Cu or Zr_7Cu_{10} in quenched Zr-Cu alloys are smaller than in the non-heat-treated Zr-Cu alloys. Therefore, the hardness of the quenched Zr-Cu alloys shows little change with varied composition. In addition, the hardness of quenched Zr-Cu alloys is higher than the values of non-heat-treated Zr-Cu alloys. The dislocation density in the Zr-Cu alloy may be increased by quenching, as one mechanism for increased

Fig.7 Relationship between Vickers hardness of the near-equiatomic Zr-Cu alloys and Zr concentration. Results of quenched Zr-Cu alloys.

hardening.

In general, the microstructure and hardness of near-equiatomic Zr-Cu alloys vary with alloy composition and heat treatment. However, the changes in microstructure and hardness have little effect on both the MT and reverse MT temperatures. Further investigation is necessary to develop control methods for the phase-transformation temperature of Zr-Cu alloys.

4. CONCLUSION

In the present study, the effect of alloy composition and heat treatment on the material properties of near-equiatomic Zr-Cu alloys. Following results were obtained. (1) It was found that the microstructures of near-equiatomic Zr-Cu alloys vary with alloy composition and heat treatment. Especially, quenching restricts the decomposition of ZrCu (P) to Zr_2Cu and/or Zr_7Cu_{10} , and enhances the martensitic transformation. (2) Martensitic transformation temperatures (A_s , A_f , M_s and M_f) of both non-heat treated and quenched Zr-Cu alloys varies little with alloy composition.

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