RAPID PUBLICATION

Amorphous (Zr-Y)₆₀Al₁₅Ni₂₅ Alloys with Two Supercooled Liquid Regions

Tao Zhang*, Akihisa Inoue**, Sujun Chen*
and Tsuyoshi Masumoto**

An amorphous phase exhibiting two distinguishable supercooled liquid regions was found in quaternary (Zr-Y)₆₀Al₁₅Ni₂₅ alloys in which the main constituent elements of Zr and Y are immiscible in a solid state. The first- and second-stage supercooled liquid regions are observed in the temperature ranges of 640 to 664 K and 763 to 810 K, respectively, accompanied by the two-distinguishable exothermic peaks due to crystallization after the appearance of the supercooled liquid regions. The temperatures of the first- and the second-reactions appear to correspond to those for ternary Y₆₀Al₁₅Ni₂₅ and Zr₆₀Al₁₅Ni₂₅ amorphous alloys, respectively. The simultaneous dissolution of the immiscible Zr and Y elements is essential for the appearance of the two-stage supercooled liquid regions. From the appearance of the second-stage supercooled liquid region, it is concluded that the precipitation of the primary crystalline phase does not exert detrious influence on the appearance of the supercooled liquid region.

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I. Introduction

It is of importance for materials science and engineering to search an amorphous alloy exhibiting a wide supercooled liquid region in the temperature range below crystallization temperature (T_x) and to clarify the mechanism for the high thermal stability of a supercooled liquid at limited alloy compositions. Recently, the present authors have found that amorphous alloys in Ln-Al-TM⁽¹⁾⁽²⁾, Zr-Al-TM⁽³⁾ and Mg-Ln-M⁽⁴⁾⁻⁽⁶⁾ (Ln=lanthanide metal, TM=transition metal, M=Ni, Cu, Zn) systems exhibit a wide supercooled liquid region before crystallization as well as a large glass-forming ability which enables to produce an amorphous bulk by a conventional metallic mold casting method. The largest value of the temperature interval between glass transition temperature (T_g) and T_x , $\Delta T_x (=T_x - T_g)$ reaches as large as 127 K for Zr-Al-Ni-Cu amorphous alloys⁽⁷⁾. In the subsequent study on the compositional effect on T_g , T_x and ΔT_x for the new amorphous alloys, we found a new phenomenon in which two glass transition regions appear in Zr-Y-Al-Ni amorphous alloys. This paper is intended to present an evidence for the appearance of two supercooled liquid regions for Zr-Y-Al-Ni amorphous alloys and to examine the influence of subsequent heat treatment on the appearance of the two supercooled liquid regions.

II. Experimental Procedure

Ternary and quaternary Zr_{60-x}Y_xAl₁₅Ni₂₅ ($x=0$ to 60 at%) alloys were used in the present study. The Al and Ni compositions were chosen because the largest ΔT_x value in Zr-Al-Ni ternary system was obtained in the vicinity of 15%Al and 25%Ni. Their ingots were prepared by arc melting a mixture of pure Zr(99.9 mass%), Y(99.9 mass%), Al(99.99 mass%) and Ni(99.9 mass%) metals in a purified argon atmosphere. The compositions are nominally expressed in atomic per cent. From the master alloy ingots, ribbons with a cross section of about $0.03 \times 1 \text{ mm}^2$ were prepared by a single roller melt-spinning technique in an argon atmosphere. The amorphicity of the melt-spun ribbons was examined by X-ray diffraction and transmission electron microscopy techniques. The exothermic and endothermic reactions associated with structural relaxation, glass transition, supercooled liquid and crystallization were measured at a heating rate of 0.67 K/s with a differential scanning calorimeter (DSC).

III. Results and Discussion

Figure 1 shows the X-ray diffraction patterns of melt-spun Zr₆₀Al₁₅Ni₂₅, Zr₃₃Y₂₇Al₁₅Ni₂₅ and Y₆₀Al₁₅Ni₂₅ alloys. The diffraction patterns consist only of broad diffraction peaks and no diffraction peak corresponding to a crystalline phase is seen in the three samples, indicating that an amorphous single phase is formed in the entire composition range of Zr_{60-x}Y_xAl₁₅Ni₂₅ ($x=0$ to 60

* Graduate Student, Tohoku University, Sendai 980, Japan.

** Institute for Materials Research, Tohoku University, Sendai 980, Japan.

Fig. 1 X-ray diffraction patterns of melt-spun $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ (a), $\text{Zr}_{33}\text{Y}_{27}\text{Al}_{15}\text{Ni}_{25}$ (b) and $\text{Y}_{60}\text{Al}_{15}\text{Ni}_{25}$ (c) alloys.

at%). The K_p value defined by $2\pi \sin \theta / \lambda$ at the main broad peak was measured to be 25.54 nm^{-1} for $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$, 24.93 nm^{-1} for $\text{Zr}_{33}\text{Y}_{27}\text{Al}_{15}\text{Ni}_{25}$ and 23.78 nm^{-1} for $\text{Y}_{60}\text{Al}_{15}\text{Ni}_{25}$. Thus, the K_p value decreases systematically with the replacement of Zr by Y because of the difference in atomic size between Zr and Y. The systematic change in the K_p value indicates that Zr and Y elements have been dissolved in the amorphous phase, even though the equilibrium phase diagram of a Zr–Y binary system belongs to an immiscible type in a solid state⁽⁸⁾. The absence of a macroscopic phase separation caused by the immiscibility gap between Zr and Y elements was also confirmed from the result that no contrast revealing the phase separation was seen over the whole cross sectional micrograph obtained with an optical microscope.

Figure 2 shows the DSC curves of the amorphous $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$, $\text{Zr}_{33}\text{Y}_{27}\text{Al}_{15}\text{Ni}_{25}$ and $\text{Y}_{60}\text{Al}_{15}\text{Ni}_{25}$ alloys. The Zr–Al–Ni and Y–Al–Ni ternary alloys have the usual transformation behavior of amorphous solid, glass transition, supercooled liquid and crystallization. On the other hand, it should be noted that the Zr–Y–Al–Ni quaternary alloy has two distinguishable supercooled liquid regions in each temperature range of 640 to 664 K and 763 to 810 K. Considering that the T_g and T_x values are 699 and 766 K for $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ and 626 and 648 K for $\text{Y}_{60}\text{Al}_{15}\text{Ni}_{25}$, the supercooled liquid regions at the low- and the high-temperature sides seem to correspond to those for the Y–Al–Ni and Zr–Al–Ni alloys, respectively. In addition, the Zr–Y–Al–Ni amorphous alloy crystallizes through two exothermic reactions with peaks at each temperature of 692 and 833 K. These exothermic peaks correspond to those for the Y–Al–Ni and Zr–Al–Ni ternary amorphous alloys. However, the exothermic amount is measured to be 1.09 kJ/mol for the low-temperature peak and 2.46 kJ/mol for the high-temperature peak, being much larger of the latter peak corresponding to the Zr–Al–Ni amorphous alloy in spite of the nearly equal values of Zr

Fig. 2 Differential scanning calorimetric curves of amorphous $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ (a), $\text{Zr}_{33}\text{Y}_{27}\text{Al}_{15}\text{Ni}_{25}$ (b) and $\text{Y}_{60}\text{Al}_{15}\text{Ni}_{25}$ (c) alloys.

and Y contents. The clear distinction of the glass transition, supercooled liquid and crystallization into two stages allows us to expect the presence of phase separation in the amorphous structure for the quaternary amorphous alloy. However, as shown in Fig. 3, neither contrast revealing the presence of phase separation nor splitting of the halo peak is seen in the bright-field electron micrograph and selected-area diffraction pattern taken from the amorphous Zr–Y–Al–Ni alloy. This result indicates that the melt-spun Zr–Y–Al–Ni ribbon prepared by melt spinning consists of a homogeneously mixed amorphous phase within the resolution of conventional TEM and X-ray diffractometry techniques. A similar distinction of supercooled liquid into two regions was also observed for quaternary $\text{Zr}_{45}\text{Y}_{15}\text{Al}_{15}\text{Ni}_{25}$ and $\text{Zr}_{15}\text{Y}_{45}\text{Al}_{15}\text{Ni}_{25}$ amorphous alloys. Consequently, the simultaneous dissolution of immiscible Zr and Y elements is presumed to cause the appearance of the two distinguishable supercooled liquid regions.

In order to investigate the influence of the primary precipitates on the second-stage glass transition behavior of the remaining amorphous phase, Fig. 4 shows the DSC curve of the $\text{Zr}_{33}\text{Y}_{27}\text{Al}_{15}\text{Ni}_{25}$ sample heated for 10 s at 768 K which is 20 K higher than the peak temperature of the first-stage exothermic reaction. The glass transition, supercooled liquid region and exothermic peak in the first stage disappear completely after the heat treatment, accompanied by the decrease in T_g . The decrease in T_g results in a remarkable extension of the supercooled liquid region from 47 K in the as-quenched state to 97 K in the heated state. This result is in good contrast to the previous data⁽⁵⁾⁽⁹⁾ that the precipitation of primary

Fig. 3 Bright-field electron micrograph (a) and selected-area diffraction pattern (b) of an amorphous $Zr_{33}Y_{27}Al_{15}Ni_{25}$ alloy.

crystalline phase brings about the disappearance or the remarkable reduction of the supercooled liquid region. The present result also suggests the possibility of producing an amorphous alloy with a much larger ΔT_x value by controlling the crystallization behavior. The detailed structural analysis is in progress. This information is expected to shed some light on clarification of the reason for the remarkable increase in ΔT_x by the precipitation of the primary phase as well as for the appearance of the two supercooled liquid regions.

Fig. 4 Differential scanning calorimetric curve of an amorphous $Zr_{33}Y_{27}Al_{15}Ni_{25}$ alloy heated for 10 s at 768 K.

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