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CHARACTERIZATION AND PROPERTIES OF NANOCRYSTAL-FORMING Zr-BASED BULK METALLIC GLASSES

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Abstract. The transformation behavior of Zr-Al-Ni-Cu-Pd metallic glasses is investigated. It is well known that the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ metallic glass has a high glass-forming ability, which is enable us to produce the glassy sample with a bulky shape. In the initial transformation stage of the alloy, the metastable fcc-Zr_2Ni phase is precipitated. Since the fcc-Zr_2Ni phase contains several icosahedral clusters in the unit cell, it is strongly correlated with the icosahedral local structure in the glassy state. By substitution of Pd with Cu, the primary phase changes into nanoscale icosahedral quasicrystalline phase. It is found that the nucleation frequency increases drastically with Pd addition, which results in the formation of nanostructured materials. These nanoscale structure control based on the glassy alloys is expected to exhibit unique mechanical properties such as a high strength and good ductility.

1. INTRODUCTION

Recently, a number of bulk metallic glasses with extremely high glass-forming ability (GFA) were reported in Zr-based multicomponent alloy systems [1,2]. They have attracted much attention in the aspects of the scientific interests in a high stability of glassy state [3]. More recently, it is found that various nanocrystalline phases are formed as a primary precipitation phase from a glassy state [4,5]. Especially, formation of nanoscale metastable phase such as nano icosahedral quasicrystalline phase (I-phase) is important for the investigation of mechanism of high GFA as well as the improvement of mechanical properties [6,7]. In these ten years, it has been reported that a nano I-phase was formed in the Zr-Al-Ni-Cu based metallic glasses with a wide supercooled liquid region and high GFA [8,9]. More recently, Chen *et al.* have found that a nano I-phase precipitates as a primary precipitation phase in a $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Ag_5$ glassy alloy [10]. The authors have reported that an I-phase with nano meter scale is formed in the $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}M_5$ (M=Pd, Au or Pt) metallic glasses [11]. In this paper, we present the effect of Pd on the formation of the nano I-phase in the aspects of the change in the nucleation and grain growth rates with Pd content in the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5-x}Pd_x$ (x=5, 10, 17.5) metallic glasses. In these studies, we intend to investigate the formation mechanism of metastable nano(quasi) crystalline phases correlated with their high stabil-

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ity of glassy state. Moreover, the improvement of mechanical properties with the formation of nanocrystal will be reported. These results lead us to the conclusion that it is very useful for the formation of new nanostructured materials based on the metallic glasses.

2. EXPERIMENTAL

The ribbon samples of $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5-x}Pd_x$ (x=0, 5, 10, 17.5) metallic glasses with a cross section of 0.03x1 mm^2 were produced by the melt-spinning technique from alloy ingots prepared by arc melting in an argon atmosphere. The thermal stability of as-prepared ribbons was measured by differential scanning calorimetry (DSC) at a heating rate of 0.67 Ks^{-1}. Isothermal decomposition was performed in the DSC equipment at the crystallization temperature, T_x for various annealing times. The heating to each isothermal temperature was performed at a high heating rate of 1.67 Ks^{-1} to prevent from a thermal influence during heating. The structure of annealed samples was examined by X-ray diffractmetry with Cu K_α radiation and nano beam electron diffraction with a beam diameter of approximately 2.4 nm. The grain size was measured by field-emission transmission electron microscopy (JEOL JEM 3000F) with an accelerating voltage of 300 kV. The mechanical test was performed in the bulk metallic glass with a cylindrical shape in 3 mm diameter.

3. RESULTS AND DISCUSSION

The DSC measurements were performed for the ribbon samples of $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5-x}Pd_x$ (x=0, 5, 10, 17.5) metallic glasses. The DSC curves changes drastically by addition of Pd. In the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ (x=0) metallic glass, a sharp single exothermic reaction appears after the significant supercooled liquid region over 100K, where the supercooled liquid region is defined as the temperature interval between the glass transition and crystallization. Although the glass transition still appears in the Pd-containing alloys, it decreases with an increase of Pd content. A single sharp exothermic peak in the non Pd-containing alloy is clearly separated into two exothermic peaks by the addition of Pd. The onset temperature of the first exothermic peak, T_x is approximately 740K for x=0, 720K for x=5, 705K for x=10 and 730K for x=17.5. The temperature interval between the first and second exothermic peaks increases with an increase of Pd content. The interval of peak temperatures of the two exothermic peaks is 45K for the 5 at.% Pd, 102K for the 10 at.% Pd and 119K for the 17.5 at.% Pd. It seems that the precipitated phase by the first exothermic reaction is stabilized with increasing Pd content. The XRD patterns of the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5-x}Pd_x$ (x=0, 5, 10, 17.5) glassy alloys annealed at T_x for short annealing time indicate the formation of an fcc Zr_2Ni phase for x=0 and an I-phase for x=5 to 17.5 at.%. It is well known that the fcc Zr_2Ni phase has a large lattice constant of a=1.23 nm [12] and several icosahedral clusters in the unit cell [13]. The formation of both phases is also confirmed by the electron diffraction method in the TEM observation.

The growth and nucleation rates of the primary phase in the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5-x}Pd_x$ (x=0, 5, 10 and 17.5) alloys are shown in the Figs. 1a and 1b, respectively. Fig. 1a shows the change in the maximum diameter of the primary phase with annealing time at T_x in the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5-x}Pd_x$ (x=0, 5, 10 and 17.5) metallic glasses. The maximum diameter is determined for the average value of five data points in the bright-field TEM images for the samples with various annealing times. The change in the maximum diameter of the primary phase is almost linear with annealing time. The calculated grain growth rate of the I-phase at the initial transformation stage decreases with increasing Pd content, where the growth rate is $4.5 \cdot 10^{-9}$ ms^{-1} for x=5, $1.7 \cdot 10^{-9}$ ms^{-1} for x=10 and $7.3 \cdot 10^{-10}$ ms^{-1} for x=17.5. The accuracy of the evaluated growth rate is approximately ±10%. In contrast, the growth rate of the Zr_2Ni phase (at x=0) is $1.1 \cdot 10^{-8}$ ms^{-1}, which is approximately 10 times larger than those of the I-phase. Thus, it is found that the Pd element is effective for the restraint of grain growth. The decrease of growth rate of the primary phase is also confirmed by the addition of Ag into the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ glassy alloy [14]. We suggest that the low growth rate is probably due to the increase of strong atomic pair of Zr-noble metal with increasing the noble metal content, which restrains the rearrangement of constitutional elements for grain growth.

Since the homogeneously distributed icosahedral particles as well as the Zr_2Ni particles in the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5-x}Pd_x$ (x=0, 5, 10 and 17.5) metallic glasses are observed in the TEM images [15], it is suggested that the homogeneous nucleation is a dominant mode for the transformation of the alloys. For the phase transformation with an isotropic constant growth rate, u and the homogeneous nucleation under a steady state condition, the volume fraction transformed, y during isothermal annealing is given by [16]:

$$y = 1 - \exp(-\pi I_v u^3 t_a^4/3), \qquad (1)$$

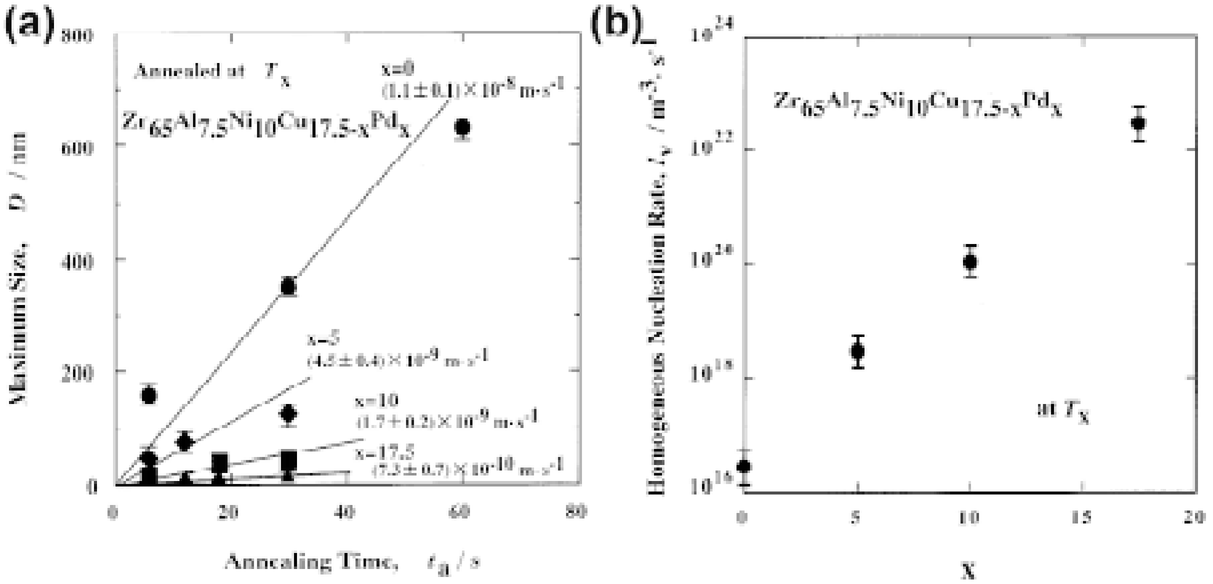

Fig. 1. Change of the maximum diameter in addition to the growth rate with annealing time (a) and calculated homogeneous nucleation rate, I_v (b) with Pd content of the primary phase at T_x in the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5-x}Pd_x$ (x=0, 5, 10 and 17.5) metallic glasses.

where t_a is the isothermal annealing time and I_v is the homogeneous nucleation rate. Therefore, we can calculate I_v as follows:

$$I_v = (-3/\pi u^3 t_a^4) \times \ln(1-y). \quad (2)$$

For the calculation of I_v at T_x, a y value of 0.2 is used in the steady state, which is obtained from the DSC thermogram and u is calculated from the TEM observation shown in Fig. 1a for the growth of the fcc Zr_2Ni and I-phases in the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5-x}Pd_x$ (x=0, 5, 10, and 17.5) metallic glasses. The calculated homogeneous nucleation rate, I_v of the primary phase at T_x in the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5-x}Pd_x$ (x=0, 5, 10, and 17.5) metallic glasses are plotted in Fig. 1b. The I_v is $(2.6\pm0.3)\cdot10^{16}$ m^{-3}s^{-1} for the precipitation of the Zr_2Ni phase at x=0. It is found that the I_v increases significantly to $(2.9\pm0.3)\cdot10^{18}$ m^{-3}s^{-1} for the precipitation of the I-phase by the addition of only 5 at.% Pd and increases almost linearly with increasing Pd content. The I_v increases to $(1.1\pm0.3)\cdot10^{20}$ m^{-3}s^{-1} for x=10 and $(2.9\pm0.3)\cdot10^{22}$ m^{-3}s^{-1} for x=17.5. The nucleation rate of the I-phase at Pd=5 at.% is nearly equal to that of the I-phase in the $Zr_{69.5}Al_{7.5}Ni_{11}Cu_{12}$ metallic glass, which contains a large amount of oxygen impurity [17].

Thus, it is concluded that the Pd is a very effective element on the decrease of the grain growth rate and the increase of nucleation rate, which is also recognized as the useful element for the formation of nanostructured materials in Zr-based metallic glasses. Considering the common local atomic configuration in the fcc Zr_2Ni and I-phases in the present alloy systems, we can suggest the icosahedral local structure in the glassy state. Since the icosahedral local atomic configuration is distorted in the fcc Zr_2Ni phase, it is implied that the Pd plays a role on the improvement of the perfection of icosahedral local order.

The stress-strain (S-S) curves in the compressive deformation at a strain rate of $5\cdot10^{-4}$ s^{-1}, at room

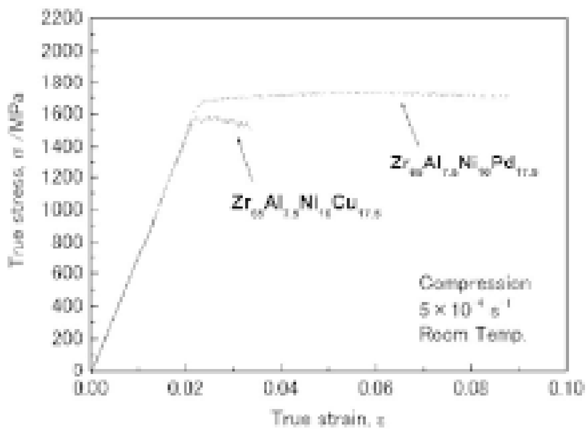

Fig. 2. Compressive stress-strain curves of the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ and $Zr_{65}Al_{7.5}Ni_{10}Pd_{17.5}$ bulk metallic glasses obtained at a strain rate of $5\cdot10^{-4}$ s^{-1} at room temperature.

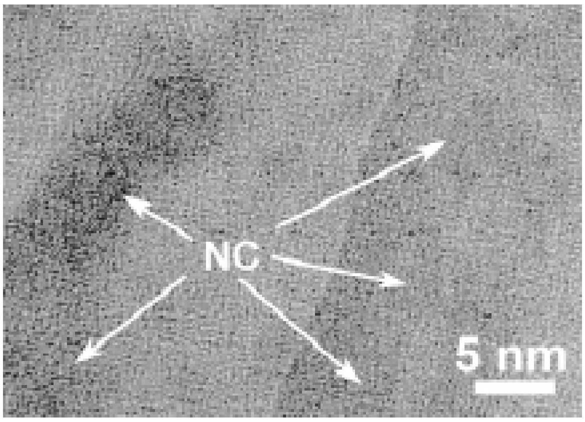

Fig. 3. High-resolution TEM (HREM) image of the facture tip of the $Zr_{65}Al_{7.5}Ni_{10}Pd_{17.5}$ metallic glass.

temperature of the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ and $Zr_{65}Al_{7.5}Ni_{10}Pd_{17.5}$ metallic glass cylinders are shown in Fig. 2. The yield stress, fracture stress and Young's modulus in the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ and $Zr_{65}Al_{7.5}Ni_{10}Pd_{17.5}$ metallic glasses are 1570 MPa, 1528 MPa, 81.5 GPa and 1594 MPa, 1698 MPa, 86.1 GPa, respectively. The yield stress is similar in both the alloys, however, the fracture strength is improved in the $Zr_{65}Al_{7.5}Ni_{10}Pd_{17.5}$ metallic glass, which is due to the significant difference in the plastic strain. It is clearly found that a complete replacement of the Pd for the Cu element in the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloy system causes drastic improvement in the plasticity. The plastic strain is estimated to be 6.6%, which is markedly improved compared with that (1.3%) in the single glassy $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ cylinder [18]. Enhancement of the plasticity in a bulk metallic glass has been achieved by dispersing various reinforcements, i.e., ceramics, ductile solid solutions and so on [19-21]. However, we confirmed a single glassy structure without secondary phases by high-resolution TEM (HREM) observation [18]. We have clarified that SEM image of the surface of the cylindrical sample near the fractured region in the $Zr_{65}Al_{7.5}Ni_{10}Pd_{17.5}$ metallic glass indicates the multi-shear band pattern at various angles from the stress axis. This is clearly in contrast with the typical images of other bulk metallic glasses that have no significant plastic strain during compressive deformation.

The microstructure feature in the fracture tip has been analyzed by TEM. Fig. 3 shows HREM image of the fractured tip of the $Zr_{65}Al_{7.5}Ni_{10}Pd_{17.5}$ metallic glass cylinder. A very unique microstructure consisting of the nanoscale 'band-like' contrast is observed. The widths of the dark and bright regions are in the ranges of 5 to 10 nm and 20 to 50 nm, respectively. We can confirm the fringe contrast in diameters of 2 to 5 nm in the dark region in the high magnification image as denoted 'NC' in the figure. The results reveal the precipitation of nanocrystalline particles. In contrast, the bright region has a homogenous maze contrast in agreement with that in the as-cast sample, indicating the fully glassy structure. The precipitated nanocrystalline particles are suggested as the metastable fcc Zr_2Ni structure by the examination of electron diffraction patterns. The significant microstructure with the precipitation of fine nanocrystalline particles arranged in the nanoscale 'band-like' region in the glassy matrix leads to the direct evidence of important phenomenon of the dynamic crystallization during the micro-shear-band propagation. As described above, the I-phase formation is observed in the static transformation, which suggests that the alloy system has a tendency to form the local icosahedral atomic configuration in the glassy state [22-24]. In the deformation-induced crystallization, icosahedral clusters are strongly distorted and the constituent elements are difficult to arrange in the icosahedral quasicrystalline order for the short time under the stress. This may be the reason for the precipitation of the fcc Zr_2Ni phase instead of the I-phase. In these studies, we conclude that the control of nanocrystalline particles precipitation brings the novel mechanical properties in the Zr-based metallic glass.

4. CONCLUSIONS

With the aim of investigating the transformation from the glassy state to the nanoscale primary phase in the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5-x}Pd_x$ (x=0, 5, 10 and 17.5) metallic glasses, the nucleation and grain growth kinetics were examined. The homogeneous nucleation rate of the I-phase is in the range of 10^{18} to 10^{22} $m^{-3}s^{-1}$. The nucleation rate strongly depends on Pd content, i.e. it increases drastically with increasing Pd content. The nucleation rate of the I-phase at x=5 is 10^2 times higher than that of the Zr_2Ni phase at x=0. It is concluded that the Pd plays an important role in the increase of nucleation site and the suppression of grain growth, which results in the formation of the nanostructured material based on the glassy alloy. The significant microstructure with the precipitation of fine nanocrystalline particles arranged in the nanoscale 'band-like' region in the glassy matrix is observed in the fracture tip in the $Zr_{65}Al_{7.5}Ni_{10}Pd_{17.5}$ bulk metallic glass. It is realized the direct evidence of important phenomenon of the dynamic crystallization during the micro-shear-band propagation. In these studies, we conclude that it is very important to control the nanostructure based on the metallic glass for the exhibition of unique mechanical properties.

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