

Deformation-Induced Nanoscale Dynamic Transformation Studies in Zr-Al-Ni-Pd and Zr-Al-Ni-Cu Bulk Metallic Glasses

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Nanoscale dynamic transformations during tensile and compressive deformation of $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ and $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ bulk metallic glasses have been investigated. Although no apparent differences are observed in the stress-strain curves in the tensile deformation between the two alloys, fine striations and depression zones with viscous flow appear at the fracture surface near the edge in the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ alloy. Unlike the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ alloy and other bulk metallic glasses, the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ bulk metallic glass exhibits a large plastic strain of approximately 7% during compressive deformation. By detailed examination of the microstructure, we provide direct evidence for nanoscale multistep shear band formation in the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ metallic glass. A novel nanoscale structure where fcc Zr_2Ni nanocrystalline particles are arranged in “bandlike” areas in the glassy matrix is observed near the compressive fracture tip. The suppression of the propagation of the shear bands due to dynamic nanocrystallization causes this structure. Furthermore, the results are recognized as a novel phenomenon, a nanoscale dynamic structural change by shear band propagation, and provide a new method for improving the mechanical properties of bulk metallic glasses. [doi:10.2320/matertrans.MF200615]

(Received November 27, 2006; Accepted March 5, 2007; Published May 25, 2007)

Keywords: metallic glasses, zirconium-based alloy, ductility, transformations, shear bands, nanocrystallization, local structure

1. Introduction

Recently, the improvement of mechanical properties such as the plasticity during deformation of bulk metallic glasses (BMGs) has been achieved by producing nanocomposite materials.^{1,2)} Furthermore, nanostructure analysis has been used to study the deformation behavior of the monolithic and nanocomposite metallic glasses to improve the mechanical properties and to understand the mechanism of the deformation processes.^{3,4)} For further development, it is necessary to produce new BMGs with good mechanical properties as well as to control the structure of nanocomposite BMGs. It is well-known that the mechanical behavior of BMGs can be classified into homogeneous and inhomogeneous deformation. Homogeneous deformation in metallic glass usually occurs at high temperatures near the glass transition temperature, T_g , accompanied with a significant plasticity.^{5,6)} Nieh *et al.* have reported that non-linear viscous flow during tensile deformation induces nanocrystallization in Zr-Al-Ti-Cu-Ni metallic glass in the supercooled liquid region, which is between 683 to 713 K.⁷⁾ In this temperature range, the diffusion of constituents occurs easily, resulting in the precipitation of nanocrystals with stable Zr_2Ni and Zr_2Cu structures. Inhomogeneous deformation, which generally appears at low temperatures such as room temperature, proceeds by the formation and propagation of localized shear bands. It is well known that fracture of BMGs generally occurs along the maximum shear stress plane (45° from the stress axis) without a significant plastic strain during compressive deformation. Numerous studies have examined the inhomogeneous deformation of metallic glasses with a variety of glass-forming abilities (GFA), *i.e.* the stability of

the glassy state, which makes it difficult to formulate a universal theory. For example, it has been reported that severe bending deformations enhance the crystallization in Al-based metallic glass ribbons with low GFA (*i.e.*, we cannot produce a bulky sample with a glassy structure).^{8,9)} It is important to understand the detailed behavior of inhomogeneous deformation in order to improve mechanical properties of BMGs with high GFA for their industrial application. Especially, deformation-induced nanoscale structure change is noted as is a new method of suppression of shear band propagation.

It has been reported that crystallization proceeds either via an increase in temperature, which is induced by localized deformations, or a change in the chemical short-range order (CSRO) in the glassy state around the shear bands in the limited condition of a very large permanent strain.^{3,10,11)} However, little is known about whether crystallization occurs dynamically during a usual inhomogeneous deformation, *i.e.* the propagation of shear bands in the BMGs with high GFA. Deformation-induced nanocrystallization during quasi-static nanoindentation has been recently reported for Zr-Cu-Ni-Al-Ti BMG.¹²⁾ However, a change in the excess free volume without any nanocrystallization in the shear bands around the microcracks has been simultaneously reported in the same alloy system.¹³⁾ Lee *et al.* have also reported a crystallization-induced plasticity during compressive deformation, which is correlated with the activation energy of crystallization in Cu-Zr-based BMGs.¹⁴⁾

Very recently, we have reported unique properties that bulk $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ metallic glass exhibits a significant plasticity in compressive deformation. This is clearly in contrast with those observed in the behavior of other BMGs.^{15,16)} We have found localized nanocrystallization in the alloy, which may be a dominant factor for plasticity.¹⁷⁾ In

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this paper, we present the deformation behavior of $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}(\text{Cu or Pd})_{17.5}$ BMGs in tension and compression. We discuss the dynamic nanoscale structural changes examined by electron microscopy and the correlation between the deformability and the local structure in the glassy state.

2. Experimental Procedures

Master ingots of $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}(\text{Cu or Pd})_{17.5}$ alloys were produced by arc-melting Zr that had 99.9% purity and Al, Ni, Cu and Pd with 99.99% purity in a purified argon atmosphere. The alloys were heated by induction melting in a quartz tube up to 1223 K in a vacuum (4×10^{-3} Pa) for the Zr-Al-Ni-Cu alloy and in a purified argon gas under the atmospheric pressure (0.1 MPa) for the Zr-Al-Ni-Pd alloy. The molten alloys were cast into a copper mold, which measured 3 mm in diameter and 50 mm long, after being thermally stabilized for 5 s at 1223 ± 3 K. The temperature of the melt was monitored using a pyrometer. Details of the preparation method have been previously reported.¹⁵⁾ The oxygen content of the as-cast cylinders was chemically analyzed to be approximately 200 mass ppm. The structure and thermal properties were examined by x-ray diffraction (XRD) with Cu K α radiation (40 kV-40 mA) and differential scanning calorimetry (DSC) with a heating rate of 0.67 K s^{-1} . Mechanical tests in tension and compression were conducted at room temperature with strain rates of $1.5 \times 10^{-4} \text{ s}^{-1}$ and $5 \times 10^{-4} \text{ s}^{-1}$, respectively. The dimensions of the tensile specimens were 11 mm in gauge length, 2 mm in gauge width, 2 mm in gauge thickness, and 2 mm in shoulder radius. Specimen surfaces were mechanically ground with silicon carbide papers up to #3000 and polished with 1 μm alumina slurry. Samples used in the compression tests were 3 mm in diameter and 6 mm in height. The fracture surface was examined by scanning electron microscopy (SEM) with an accelerating voltage of 20 kV. The fractured samples were cut and polished to obtain approximately 5 μm -thick fracture surfaces. The samples were ion-milled from the polished surface, *i.e.*, the opposite side of the fractured surface, with liquid nitrogen cooling using low-angle ion milling and a polishing facility for transmission electron microscopy (TEM) observations. The fracture surface was also slightly ion-milled with a very low energy to remove the surface oxide film and contamination. TEM observations were performed using a field-emission-type microscope (JEOL JEM-3000F) with an accelerating voltage of 300 kV. The structures of the precipitates were analyzed by selected-area electron diffraction (SAD) taken from a region that measured approximately 0.5 μm in diameter, and by nanobeam electron diffraction (NBD) with a beam diameter of 2.4 nm. The structure of the local region was also analyzed using the fast Fourier transform of the high-resolution image.

3. Results and Discussion

3.1 Structure and mechanical properties of Zr-Al-Ni-(Cu or Pd) BMGs

Figures 1(a) and 1(b) show XRD patterns and DSC curves of the as-cast samples, respectively. No significant diffraction

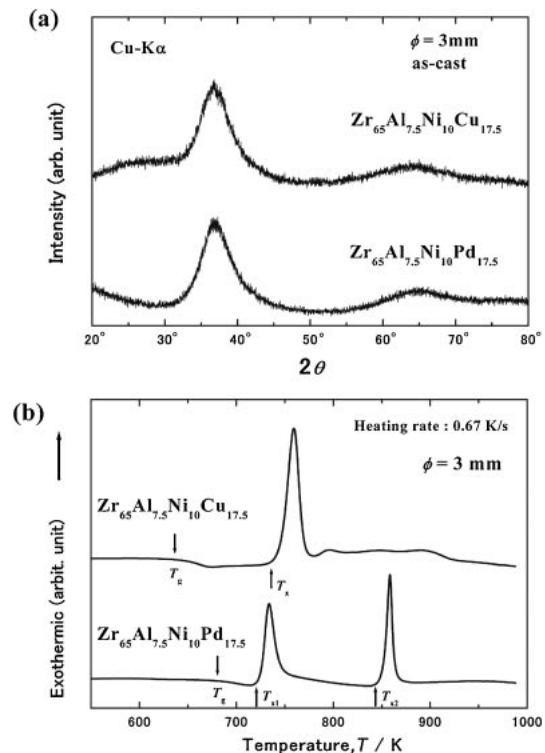


Fig. 1 X-ray diffraction (XRD) patterns (a) and differential scanning calorimetry (DSC) curves (b) of the as-cast $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ and $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ BMGs, of 3 mm in diameter.

peaks except the halo pattern, are observed in the two XRD patterns in (a). The DSC curves in (b) exhibit a significant glass transition and a wide supercooled liquid region before crystallization for both alloys. The glass transition temperature, T_g , and the supercooled liquid region, ΔT_x , which is defined as the interval between the onset temperature of the glass transition and the first crystallization, are 635 K and 102 K for the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ alloy and 684 K and 38 K for the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ alloy, respectively. Crystallization proceeds through a single crystallization peak in the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ alloy. In contrast, a two-stage crystallization reaction is observed in the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ alloy, which is the same transformation behavior observed in the melt-spun ribbons.¹⁸⁾ The heat of crystallization is 4.2 kJ mol^{-1} for the single peak in the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ alloy, 1.9 kJ mol^{-1} for the first peak and 2.1 kJ mol^{-1} for the second peak in the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ alloy. We have previously reported that the icosahedral quasicrystalline phase (I-phase) is formed in the first peak of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ alloy,¹⁸⁾ and that the two-stage crystallization reaction consists of the precipitation of fcc Zr_2Ni as the primary phase and the formation of tetragonal Zr_2Ni and Zr_6NiAl_2 phases with the decomposition of fcc Zr_2Ni , even in the apparently single exothermic peak of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ alloy.¹⁹⁾ Figure 2 shows bright-field (BF) TEM images and SAD patterns of the as-cast $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ ((a) and (b)) and $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ ((c) and (d)) alloys, respectively. The BF images ((a) and (c)) do not have significant contrast and the SAD patterns ((b) and (d)) consist of only a halo ring. Figure 3 shows high-resolution TEM (HREM) images of the as-cast $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ (a) and $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ (b) alloys.

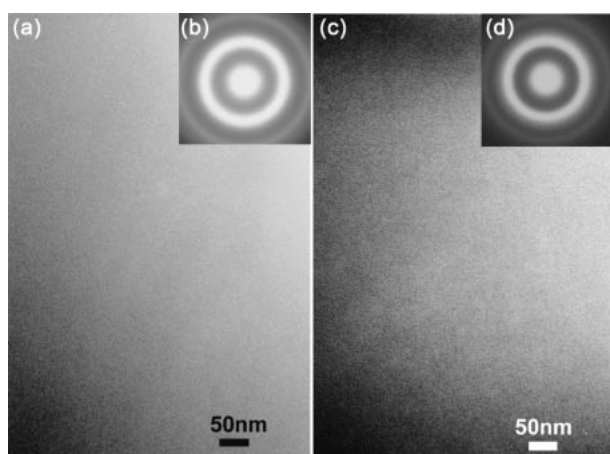


Fig. 2 Bright-field transmission electron microscopy (TEM) images and selected-area electron diffraction (SAD) patterns of the as-cast $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ ((a) and (b)) and $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ ((c) and (d)) BMGs, of 3 mm in diameter.

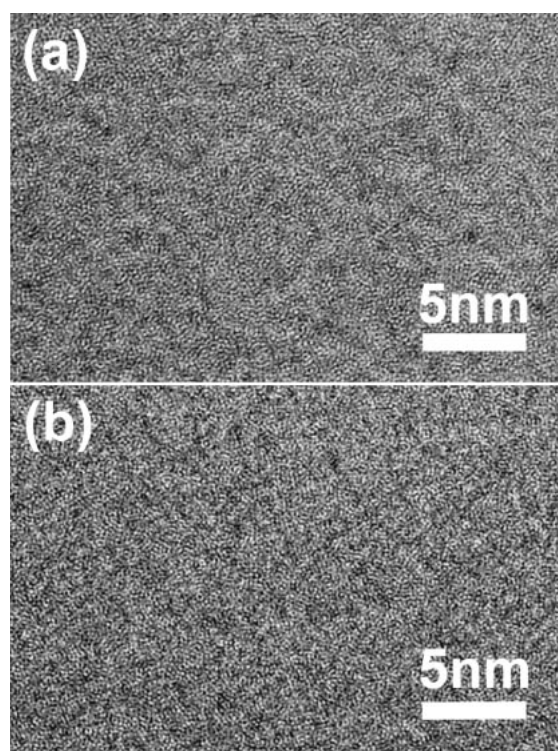


Fig. 3 High-resolution TEM (HREM) images of the as-cast $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ (a) and $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ (b) BMGs, of 3 mm in diameter.

Homogeneous maze contrast is observed and no obvious fringe contrast, which would reflect a crystalline structure, is seen in the HREM images. These observations indicate that the as-cast alloys have homogeneous glassy structures and the microstructures of the two alloys do not significantly differ from each other.

Figure 4 shows stress-strain (S-S) curves of the tensile (a) and compressive (b) deformation of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ and $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ metallic glasses. In the tensile deformation (Fig. 4(a)), Young's modulus and the yield stress of the two alloys are nearly equal. For example, the yield stress is 1300 MPa in the Zr-Al-Ni-Pd alloy and

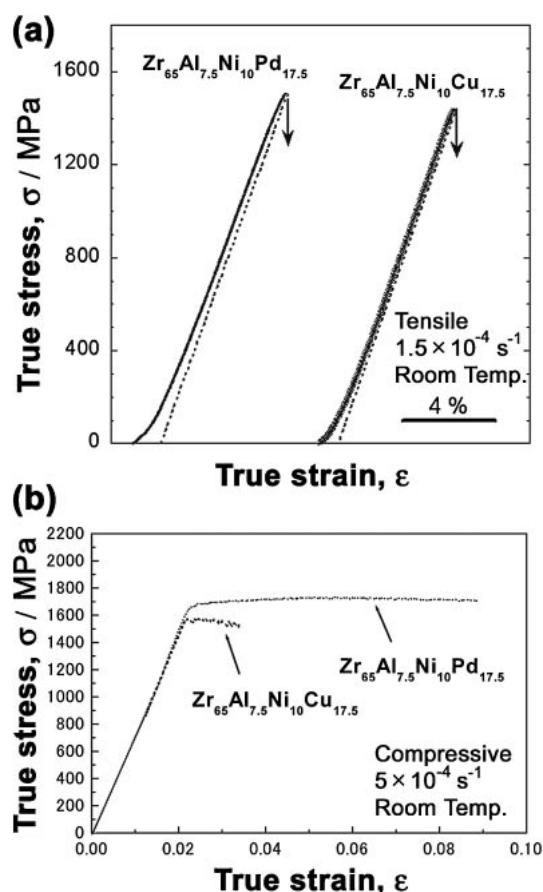


Fig. 4 Tensile (a) and compressive (b) stress-strain curves of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ and $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ BMGs at room temperature at strain rates of $1.5 \times 10^{-4} \text{ s}^{-1}$ and $5 \times 10^{-4} \text{ s}^{-1}$, respectively.

1320 MPa in the Zr-Al-Ni-Cu alloy. In contrast, the fracture stress and the plastic elongation of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ alloy (1500 MPa and 0.2%, respectively) are larger than those of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ alloy (1450 MPa and less than 0.1%, respectively). These results suggest that the alloys have different fracture modes. As shown in Fig. 4(b), the deformation behavior of the alloys during compression significantly differs between two alloys. The yield stress, fracture stress, and Young's modulus of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ metallic glass are 1590 MPa, 1700 MPa, and 86.1 GPa, respectively, which are higher than those of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ metallic glass (1570 MPa, 1530 MPa and 81.5 GPa, respectively). However the plasticity exhibits a more important difference. The plastic strain of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ metallic glass is estimated to be 6.6%, which is markedly larger than that (1.3%) of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ alloy. In most monolithic metallic glasses, the plastic deformation is approximately a few %.^{5,20} Hence, $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ metallic glass has an exceptionally high plasticity.

3.2 Deformation modes of Zr-Al-Ni-(Cu or Pd) BMGs

Improving the mechanical properties for industrial applications has received much attention in recent studies of BMGs. It is well known that nanocomposite materials, which are based on nanoscale structure controlled BMGs, exhibit significant mechanical strength and plasticity.^{21–24} In particular, the nanoscale inhomogeneity effectively improves the

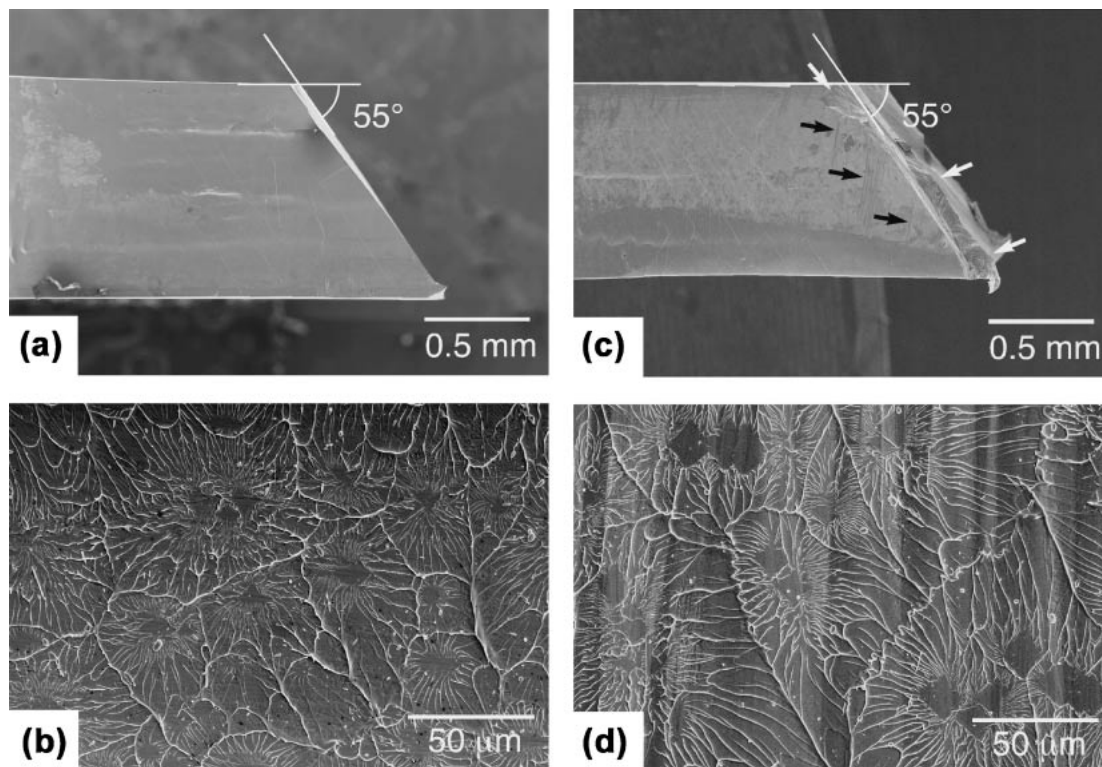


Fig. 5 Scanning electron microscopy (SEM) images of the side view in the tensile fractured specimen and fracture surface of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ ((a) and (b)) and $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ ((c) and (d)) BMGs.

plasticity by suppressing the propagation of shear planes during deformation. From this viewpoint, nanoscale dynamic crystallization and local phase separation around shear bands have been studied along with annealing to control the nanostructure.²⁵⁾ To clarify the mechanism of such a dynamic structure change in BMGs with high GFA, we have performed a comparative nanoscale structural analyses of the present alloys after deformation.

As shown in Fig. 4(a), the two alloys exhibit slight differences in the fracture strength and the plasticity even during tensile deformation, suggesting different deformation modes. Figure 5 shows side view SEM images of the tensile fracture surface of $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ (a) and $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ (b) metallic glasses. Similarly to other BMGs, the fracture surface is inclined from the tensile axis by approximately 55° in both alloys.^{3,26)} While similar vein patterns are observed in the fracture surfaces of $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ (Fig. 5(c)) and $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ (Fig. 5(d)), viscous flow areas marked by white arrows in (c) as well as fine shear bands shown by the black arrows in (c) are observed near the fracture edge in the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ alloy. To clarify the differences in the fracture mode between the two alloys, detailed examinations of the areas around the fracture edge were performed. Figure 6 shows SEM images of areas around the edge of the specimen surfaces at the point of failure where the initial crack propagation and viscous flow deformation occurred. The fracture edge is very smooth in the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ alloy (Fig. 6(a)), whereas depression zones are observed in the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ alloy, which are indicated by white arrows in (b). We have previously reported that depression zones can penetrate more

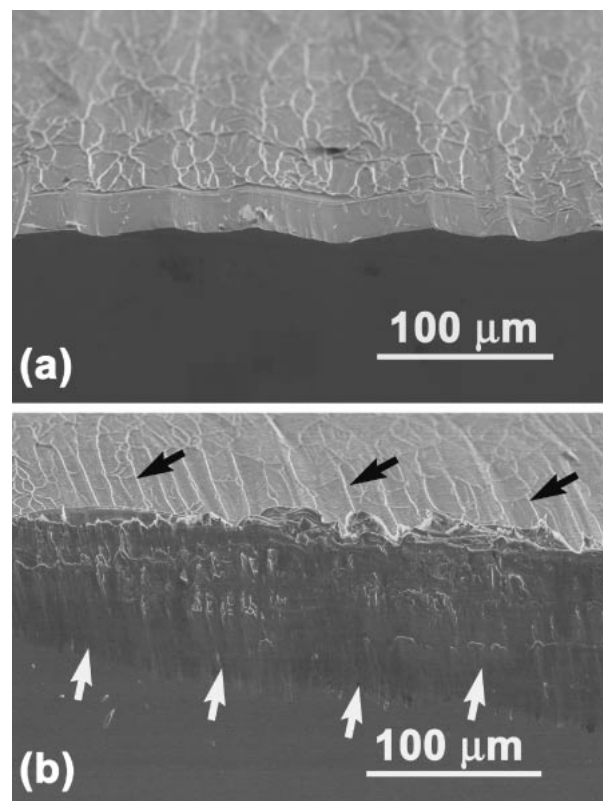


Fig. 6 SEM images of the edge of surface at the point of failure in the tensile fractured specimen of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ (a) and $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ (b) BMGs.

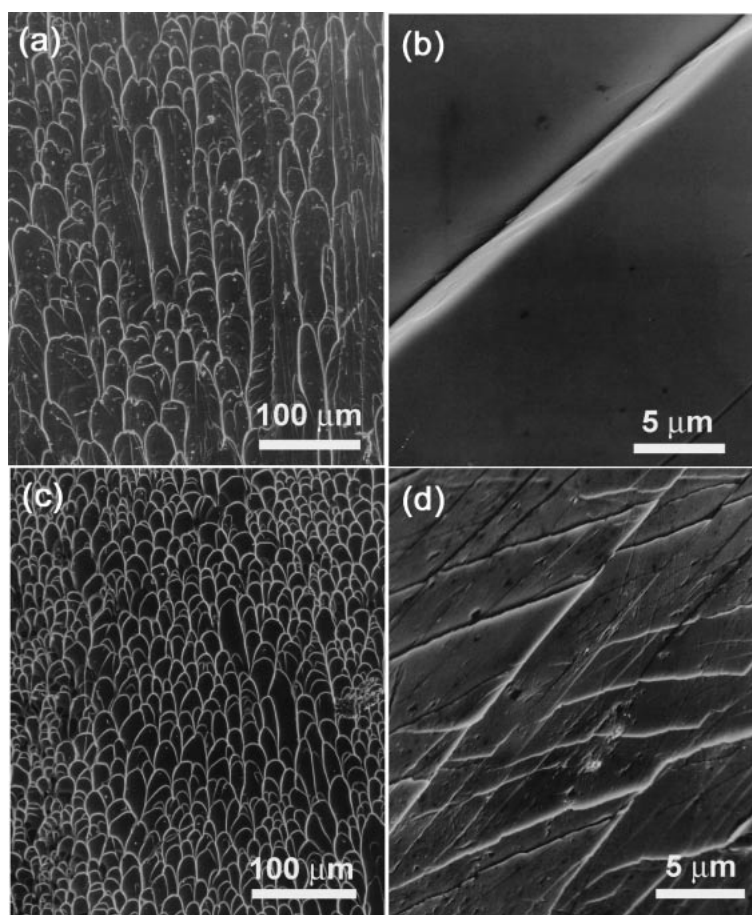


Fig. 7 SEM images of fracture surface and cylindrical sample surface near fractured area, which show shear bands of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ ((a) and (b)) and $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ ((c) and (d)) BMGs.

than $50\text{ }\mu\text{m}$ deep.²⁷⁾ Thus, we hypothesize that the depression zones in the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ alloy are formed by viscous flow deformation at the initial crack propagation, which is consistent with the results that striations as well as vein patterns appear near the edge (black arrows in Fig. 5(b)). In contrast, the corresponding area is roughly rippled and relatively smooth in the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ alloy. These features indicate different deformation modes for the two alloys.

A further remarkable difference is observed in the fracture structure in the compressive deformation. Figure 7 shows SEM images of the fracture surface and a surface of the cylindrical sample near the compressively fractured region in the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ ((a) and (b)) and $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ ((c) and (d)) metallic glasses, respectively. Both alloys display typical vein patterns in the fracture surface. However, the veins in the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ metallic glass (Fig. 7(a)) are finer than those in the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ metallic glass (Fig. 7(c)). The finer vein size suggests a different fracture mode originated from the lower stability of the supercooled liquid state during the viscous flow in the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ metallic glass compared to that in other BMGs as well as the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ metallic glass. Figures 7(b) and (d) indicate that the number density of shear bands is different between the alloys. In the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ metallic glass, shear bands are formed approximately 45° to the direction of compression, which corresponds to the maximum shear

plane. The compressive deformation proceeds through the propagation of a single shear band or a few shear bands; because we thus observed only major shear bands. The distance between shear bands is greater than $20\text{ }\mu\text{m}$. In contrast, in the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ metallic glass, a multi-shear-band pattern is obtained in the surface near a fractured area (Fig. 7(d)), where a large number of shear bands are separated less than $1\text{ }\mu\text{m}$ from each other. While the primary shear bands have similar directions to the maximum shear plane, other numerous shear bands appear at various angles from the stress axis. These findings clearly disagree with typical images of other BMGs and the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ metallic glass shown in Fig. 7(b), which do not have a significant plastic strain during compressive deformation. A multi-shear-band pattern is usually observed in a multiaxial stress state such as indentation.²⁸⁾ In the present study, deformation proceeds under a uniaxial stress. Although a similar multi-shear-band is obtained in nanocomposite materials, which consist of nanocrystalline particles or a ductile crystalline phase in a glassy matrix under a uniaxial stress,^{29–31)} this multi-shear-band does not appear in monolithic BMGs with a high GFA, except for Pt-Cu-Ni-P BMG, where the ductility is believed to be related to the high Poisson ratio.³²⁾ Hence, we speculate that a dynamic crystallization in the Zr-Al-Ni-Pd alloy suppresses the propagation of the shear band, leading to a significant deformation ($\sim 6.6\%$). Under these conditions, enhanced

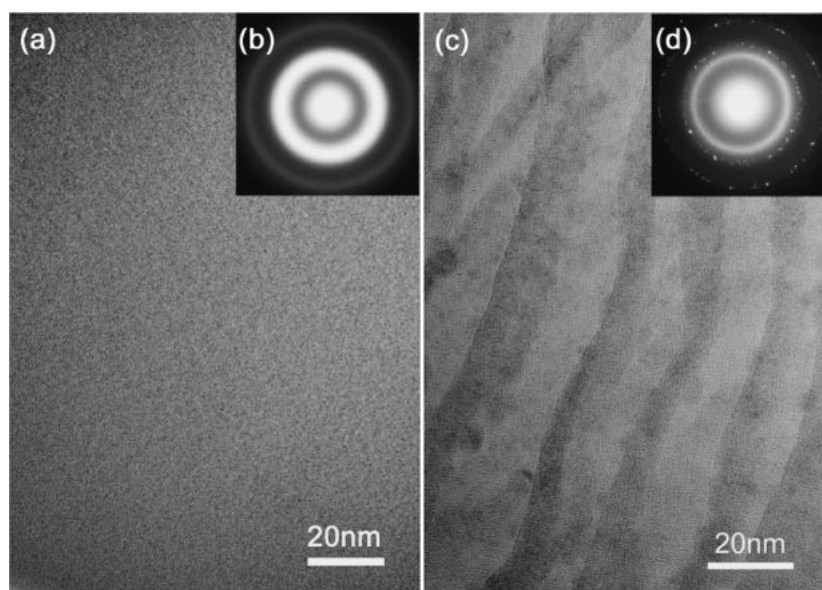


Fig. 8 HREM images and SAD patterns taken from the entire area around the fracture tip of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ ((a) and (b)) and $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ ((c) and (d)) BMGs.

shear band nucleation and a slight deviation of shear band propagation from that in the initial state with the progress of deformation are expected, resulting in multi-shear-band formation with several angles. Moreover, we note the possibility that various local stress-states may develop in the areas around the cross points of shear bands.

3.3 Microstructure characterization in deformed BMGs

The unique features of the fracture surface of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ alloy deformed in tension may be attributed to microstructural changes. The authors have reported the structure of the tensile fracture surface of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ BMG analyzed by microbeam x-ray diffraction measurements.³³⁾ Although no significant changes in the XRD profile such as crystallization were observed and the glassy structure remained macroscopically during tensile deformation, it was found that the halo reflection taken from the fracture surface was sharper than that in the as-cast state. This suggests that microstructural changes such as clustering or nanocrystallization occurred during crack propagation. In order to thoroughly analyze the microstructural changes near the fracture tip in compressively deformed alloys, TEM observations were performed.

Figure 8 shows HREM images and SAD patterns near the fractured tip of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ ((a) and (b)) and $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ ((c) and (d)) alloys, respectively. The HREM image of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ alloy (Fig. 8(a)) shows no obvious differences from the as-cast sample, where only a homogeneous maze contrast is observed. Also the SAD pattern (b) exhibits only a halo pattern without diffraction spots. These results indicate that the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ metallic glass remains completely glassy after the compressive deformation. In Fig. 8(c), a very unique microstructure that consists of a nanoscale “bandlike” contrast, is observed near the fractured tip of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ metallic glass. The widths of the dark and bright regions range between 5 to 10 nm and 20 to 50 nm, respectively. This

image significantly differs from that of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ metallic glass. The SAD pattern indicates a halo ring in addition to Debye spots, which may be caused by coexisting glassy and crystalline structures.

To identify the “bandlike” image, detailed HREM observations and nanoscale structural analyses were conducted. Figure 9 shows HREM images with high magnification ((a) and (b)), fast Fourier transform (FFT) (c), NBD (d) and SAD (e) patterns near the fractured tip of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ metallic glass cylinder. Nanocrystalline particles with diameters between 2 and 5 nm, which are denoted as “NC” in the dark region in Fig. 9(a), are observed. In contrast, the bright region exhibits a homogenous maze contrast, similarly to the as-deformed and as-cast $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ metallic glass. The enlarged HREM image of the dark region (Fig. 9(b)) involves two fringe contrasts with spacings of 0.197 nm and 0.238 nm. The FFT (Fig. 9(c)) obtained from the bright region in Fig. 9(a) exhibits a halo pattern, indicating a fully glassy structure. The precipitated nanocrystalline particles are identified as metastable fcc Zr_2Ni by the NBD pattern (Fig. 9(d)) and the SAD pattern (Fig. 9(e)). The fringe spacings observed in (b) match well with the (531) and (333) interplanar spacings of the fcc Zr_2Ni . The fcc Zr_2Ni structure is a well known unique structure, which contains distorted icosahedral clusters in the large unit cell with the lattice parameter of approximately 1.23 nm.^{34–36)} The unique microstructure with the precipitation of fine nanocrystalline particles arranged in the nanoscale “bandlike” region in the glassy matrix, provides direct evidence for dynamic crystallization during micro-shear-band propagation. The precipitation of nanocrystalline particles induced by micro-shear-band propagation can be observed in several samples of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ metallic glass during compressive deformation. However, we did not observe nanocrystalline particles in the samples deformed in tension; the density of micro-shear-bands might be too low.

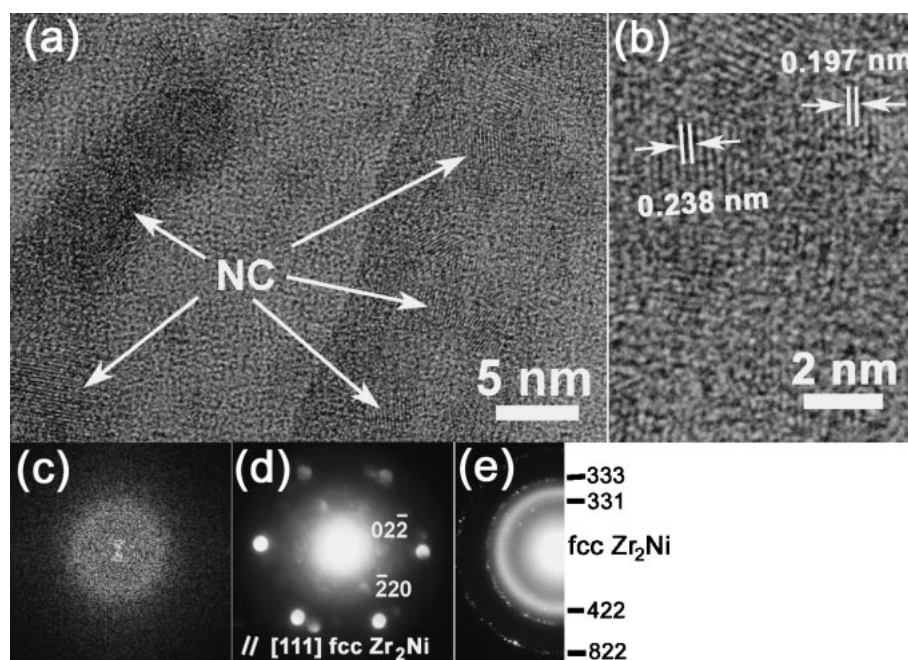


Fig. 9 HREM images of the nanocrystalline particles precipitated in nano-multistep shear bands around the fracture tip of $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ metallic glass ((a) and (b)). The fast Fourier transform (FFT) (c) obtained from the bright region and nanobeam electron diffraction (NBD) pattern (d) taken from the dark region in the HREM image of (a) and selected-area electron diffraction pattern as identified as the fcc Zr_2Ni structure (e).

3.4 Deformation mechanism of Zr-Al-Ni-(Cu or Pd) BMGs

At the initial stage of plastic deformation, a shear band begins to move under the shear stress associated with localized viscous flow, which is a typical deformation mechanism in metallic glasses. As the shear band propagates, segregation and transformation are induced by local temperature increase or by a change in CSRO, which are caused by the concentration of shear stress. The stability of the supercooled liquid state in the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ metallic glass is lower than $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$, as indicated by the narrower supercooled liquid region in Fig. 1(b). Thus, shear band propagation induces the transformation in the supercooled liquid state more easily in the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ alloy. We have previously reported that static annealing gives rise to precipitation of the I-phase in the primary transformation stage in $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ metallic glass.³⁷⁾ The I-phase is directly formed in the as-cast cylinder prepared at a lower cooling rate as shown in the XRD patterns in Fig. 10, where the diffraction peaks characterized as the I-phase are clearly observed in the bulk sample of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ alloy of 6 mm in diameter. These results suggest the existence of stable icosahedral local order in the supercooled liquid state of the alloy.^{38–40)} However, no I-phase is detected in the fractured surface. In deformation-induced crystallization, the metallic glass is strongly distorted around a shear band and it is difficult for the constituent atoms to arrange themselves into icosahedral quasicrystalline order in a short time under stress. This could be the reason why the fcc Zr_2Ni phase containing distorted icosahedral clusters precipitates instead of the I-phase. A similar tendency has been reported in mechanically disordered $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{12.5}\text{Pd}_5$ metallic glass by ball-milling, where the primary phase changes from

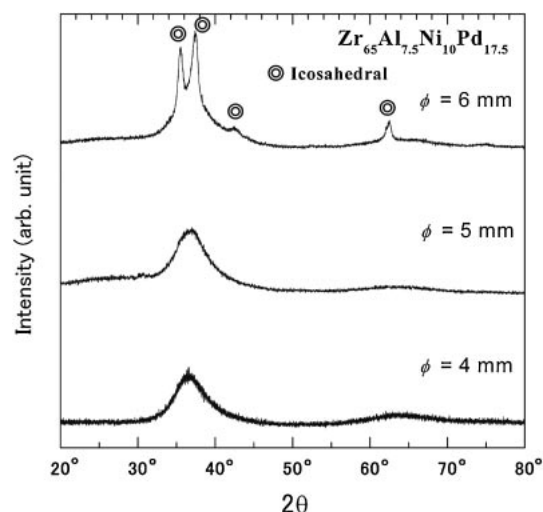


Fig. 10 XRD patterns of the as-cast $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ BMG of several diameters.

the I-phase into the fcc Zr_2Ni phase.⁴¹⁾

By the precipitation of the fcc Zr_2Ni nanocrystalline particles, the propagation of a shear band is arrested because localized viscous flow is suppressed, which results in nanocrystals arranged along a stationary shear band. Then, another shear band begins to move near the region where the previous shear band was stopped because of the local concentration of shear stress. By repeating this process, *i.e.*, shear band branching and retardation of a crack initiation, a significant plasticity is achieved. This is the mechanism to form nanoscale multisteps of shear bands. In contrast, the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ BMG does not exhibit such dynamic transformation during shear band propagation as the stability

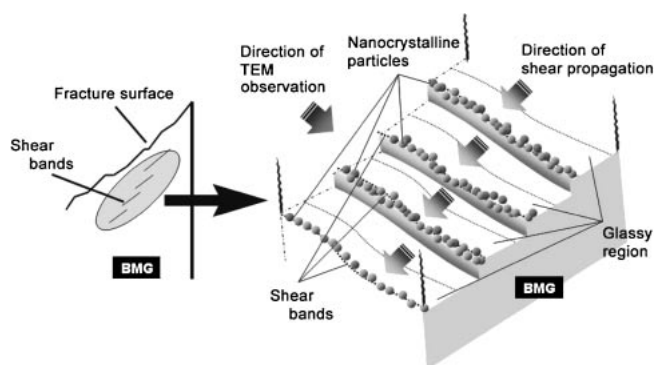


Fig. 11 Schematic illustration of the formation mechanism of the nano-scale “bandlike” structure based on multistep shear bands around the fracture surface. Multistep shear bands are formed by shear bands branching before the initiation of a crack. Arrow indicates the direction of TEM observation, and the glassy and nanocrystalline regions should be arranged in the “bandlike” structure consistent with the HREM images.

of the supercooled liquid state is high. The formation of multi-shear-bands by localized dynamic crystallization occurs more easily under compressive deformation than under tensile deformation because the external stress enhances the preparation of a crack from the initial shear band in the latter. Figure 11 schematically illustrates shear band propagation before the initiation of a crack around a fracture surface where the direction of the TEM observation is indicated by the arrow. From this direction, the glassy and nanocrystalline regions should be arranged in a “bandlike” structure, which is consistent with the TEM images. We estimate that the shear bands can move for approximately 20 to 50 nm in the glassy region without nanocrystallization.

4. Conclusion

We have investigated the tensile and compressive deformation behavior of two Zr-based BMGs, $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ and $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$, with an emphasis on the nanoscale dynamic transformation during deformation. Fine striations and significant depression zones by viscous flow appear at the fracture surface near the edge in the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ alloy. While the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ BMG shows only a few % plastic strain, which is the typical deformation behavior of BMGs, the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ BMG exhibits a significant plastic strain of approximately 7% during the compressive deformation. The plasticity of the latter originates from the formation of nanoscale multistep shear bands during deformation. The detailed analysis around the fracture surface by electron microscopy provides evidence for a deformation-induced microstructural change. A novel nanoscale structure where fcc Zr_2Ni nanocrystalline particles are arranged in “bandlike” zones formed in the glassy matrix is observed near the fracture tip in the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ alloy. It is concluded that the nanoscale “bandlike” structure results from the suppressed propagation of the shear bands, which is due to dynamic nanocrystallization. We speculate that the icosahedral local structure is associated with the precipitation of fcc Zr_2Ni nanocrystalline particles in the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ alloy. The present results are recognized as a novel phenomenon where shear band propagation causes a nano-

scale dynamic structural change, which may be a new method to improve the mechanical properties of BMGs.

Acknowledgments

We thank Prof. H.S. Chen for the stimulating discussions. This work has been supported by a Grant-in-Aid of the Ministry of Education, Culture, Sports, Science and Technology of Japan, Priority Areas on “Materials Science of Bulk Metallic Glasses” and Japan Society for the Promotion of Science (JSPS) Asian Core Program.

REFERENCES

- 1) C. C. Hays, C. P. Kim and W. L. Johnson: *Phys. Rev. Lett.* **27** (2000) 2901–2904.
- 2) G. He, J. Eckert, W. Löser and L. Schultz: *Nature Mater.* **2** (2003) 33–37.
- 3) C. T. Liu, L. Heatherly, D. S. Easton, C. A. Carmichael, J. H. Schneibel, C. H. Chen, J. L. Wright, M. H. Yoo, J. A. Horton and A. Inoue: *Met. Mater. Trans. A* **29A** (1998) 1811–1820.
- 4) Z. F. Zhang, J. Eckert and L. Schultz: *Acta Mater.* **51** (2003) 1167–1179.
- 5) A. Inoue: *Bulk Amorphous Alloys- Practical Characterization and Applications* (Trans Tech, Zurich, 1999).
- 6) A. S. Argon: *Acta Met.* **27** (1979) 47–58.
- 7) T. G. Nieh, J. Wadsworth, C. T. Liu, T. Ohkubo and Y. Hirotsu: *Acta Mater.* **49** (2001) 2887–2896.
- 8) H. Chen, Y. He, G. J. Shiflet and S. J. Poon: *Nature* **367** (1994) 541–543.
- 9) W. H. Jiang, F. E. Pinkerton and M. Atzmon: *Scripta Mater.* **48** (2003) 1195–1200.
- 10) H. S. Chen: *Appl. Phys. Lett.* **29** (1976) 328–330.
- 11) P. Asoka-Kumar, J. Hartley, R. Howell, P. A. Sterne and T. G. Nieh: *Appl. Phys. Lett.* **77** (2000) 1973–1975.
- 12) J. J. Kim, Y. Choi, S. Suresh and A. S. Argon: *Science* **295** (2002) 654–656.
- 13) L. Jing, F. Spaepen and F. Hufnagel: *Philos. Mag. A* **82** (2002) 2623–2630.
- 14) S. W. Lee, M. Y. Huh, E. Fleury and J. C. Lee: *Acta Mater.* **54** (2006) 349–355.
- 15) H. Kato, A. Inoue and J. Saida: *Appl. Phys. Lett.* **85** (2004) 2205–2207.
- 16) H. Kato, J. Saida and A. Inoue: *Scripta Mater.* **51** (2004) 1063–1068.
- 17) J. Saida, A.D.H. Setyawan, H. Kato and A. Inoue: *Appl. Phys. Lett.* **87** (2005) 151907–1–3.
- 18) J. Saida, M. Matsushita and A. Inoue: *Mater. Trans. JIM* **41** (2000) 1505–1510.
- 19) J. Saida, M. Matsushita and A. Inoue: *J. Mater. Res.* **16** (2001) 28–31.
- 20) H. A. Bruck, A. J. Rosakis and W. L. Johnson: *J. Mater. Res.* **11** (1996) 503–511.
- 21) A. Inoue, C. Fan, J. Saida and T. Zhang: *Sci. Tech. Adv. Mater.* **1** (2000) 73–86.
- 22) J. C. Lee, Y. C. Kim, J. P. Ahn and H. S. Kim: *Acta Mater.* **53** (2005) 129–139.
- 23) A. Inoue, W. Zhang, T. Tsurui, A. R. Yavari and A. L. Greer: *Philos. Mag. Lett.* **85** (2005) 221–229.
- 24) K. Hajlaoui, A. R. Yavari, B. Doisneau, A. LeMoulec, W. J. Botta, F. G. Vaughan, A. L. Greer, A. Inoue, W. Zhang and Å. Kvick: *Scripta Mater.* **54** (2006) 1829–1834.
- 25) J. C. Oh, T. Ohkubo, Y. C. Kim, E. Fleury and K. Hono: *Scripta Mater.* **53** (2005) 165–169.
- 26) T. Mukai, T. G. Nieh, Y. Kawamura, A. Inoue and K. Higashi: *Intermetallics* **10** (2002) 1071–1077.
- 27) K. Yoshimi, H. Kato, J. Saida and A. Inoue: *Mater. Trans.* **46** (2005) 2870–2874.
- 28) For example, A. Antoniou, A. F. Bastawros, C.C.H. Lo and S. B. Biner: *Mater. Sci. Eng.* **A394** (2005) 96–102.
- 29) L. Q. Xing, Y. Li, K. T. Ramesh, J. Li and T. C. Hufnagel: *Phys. Rev. B* **64** (2001) 180201–1–4.

- 30) J. C. Lee, Y. C. Kim, J. P. Ahn, H. S. Kim, S. H. Lee and B. J. Lee: *Acta Mater.* **52** (2004) 1525–1533.
- 31) K. B. Kim, J. Das, F. Baier and J. Eckert: *Appl. Phys. Lett.* **86** (2005) 171909-1–3.
- 32) J. Schroers and W.L. Johnson: *Phys. Rev. Lett.* **93** (2004) 255506-1–4.
- 33) K. Yoshimi, H. Kato, J. Saida and A. Inoue: *Mater. Sci. Forum*, **539–543** (2007) 2054–2058.
- 34) Z. Altounian, E. Batalla, J. O. Strom-Olsen and J. L. Walter: *J. Appl. Phys.* **61** (1987) 149–155.
- 35) Q. B. Yang: *Philos. Mag. Lett.* **57** (1988) 171–176.
- 36) J. Saida, M. Matsushita and A. Inoue: *Intermetallics* **10** (2002) 1089–1098.
- 37) A. Inoue, J. Saida, M. Matsushita and T. Sakurai: *Mater. Trans. JIM* **41** (2000) 362–365.
- 38) E. Matsubara, T. Nakamura, M. Sakurai, M. Imafuku, S. Sato, J. Saida and A. Inoue: *Mater. Res. Soc. Symp. Proc.* **644** (2001) L1.1.1–L1.1.11.
- 39) J. Saida, C. Li, M. Matsushita and A. Inoue: *J. Mater. Res.* **15** (2001) 3389–3401.
- 40) K. Saksl, H. Franz, K. Jívári, J. Saida, A. Inoue and J. Z. Jiang: *Appl. Phys. Lett.* **83** (2003) 3924–3926.
- 41) J. Saida, M. S. El-Eskandarany and A. Inoue: *Scripta Mater.* **48** (2003) 1397–1401.