Enhancement of Ductility and Plasticity of Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_5$ Bulk Glassy Alloy by Cold Rolling

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With the aim of improving ductility and plasticity of a Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_5$ bulk glassy alloy, a cold rolling treatment leading to the rolled structure with high-density slip bands was performed. A number of slip bands were introduced along the maximum shear stress plane by cold rolling, and the first slip bands were found to slant significantly with increasing reduction ratio in thickness. At the critical reduction ratios, the second slip bands were introduced at a reduction ratio of 30%, followed by the third slip bands at a reduction ratio of 60%. Mechanical properties of the rolled samples were examined by bending test and Charpy impact test. The maximum bend deflection value before failure increased with an increase of reduction ratio, indicating that the cold rolling improves the plasticity of the bulk glassy alloy. Since the Charpy impact value depends on the rolling direction, we selected an optimum rolling direction in which the maximum Charpy impact value is obtained. The control of the rolling direction causes an increase in the Charpy impact value by 36% as compared with the unrolled alloy. Consequently, the cold rolling process is concluded to be a valuable method for improving the ductility and plasticity of the bulk glassy alloy.

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1. Introduction

Recently, multiplication of alloy components has been found to improve a glass-forming ability as exemplified by Mg$_2$-$^{1}$, Ln$_2$-$^{3}$ and Zr$_3$-$^{5}$ based alloy systems. Based on the feature of their alloy components, Inoue has derived the following three empirical rules$^4$, i.e., (1) multicomponent over ternary alloy system, (2) different atomic size ratios above 12%, (3) large negative mixing enthalpy between elements. It has been reported that the glassy alloy with a composition of Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_5$ has large $\Delta T_C (= T_a - T_C)$ and $T_f/T_m$ values,$^5$ and can be produced in a cylindrical bulk form with a diameter of 30 mm.$^9$ The subsequent systematic study enables us to form a much large-scale bulk glassy alloy in Pd$_7$-$^{7}$ based system. Mechanical properties of these bulk glassy alloys are characterized as low Young’s modulus and high tensile strength. Recently, some bulk glassy alloys have already been used as commercial materials, e.g., face material of golf clubs, optical parts and so on. However, the lack of homogeneous deformation often results in inferior mechanical properties. The improvement of ductility and plasticity of bulk glassy alloys has strongly been desired for an increase in reliability.

There have been a number of data on the deformation mechanism of amorphous alloys to prove their high strength. The plastic deformation of amorphous alloys at room temperature is presumed to originate from a pseudo-melting phenomenon$^{8,9}$ in a maximum shear stress plane, because the vein pattern is usually observed on the fractured surface. The mechanism of the slip band behavior has been considered to be as follows: (1) a build up of elastic strain, (2) concentration at a maximum shear stress plane, (3) elastic strain energy change to thermal energy, and (4) rapid propagation of the pseudo melting region by the elastic energy release. The feature of the plastic deformation is called as ‘work-softening’.

This work-softening phenomenon is one of the reasons for insufficient ductility and plasticity of amorphous alloys.

The use of the work-softening phenomenon seems to be useful for the improvement of ductility and plasticity of amorphous alloys. The improvement of mechanical properties has been tried for rapidly solidified amorphous samples by cold drawing$^{10}$ (for wire shape sample) and cold rolling$^{11}$ (for ribbon shape sample). These cold-worked amorphous alloys show a significant increase of yield stress and elastic strain at yield point. Recently, Inoue et al.$^{12}$ tried cold rolling to strengthen the Zr-based bulk glassy alloy. We tried to obtain definite data on the improvement of ductility and plasticity of bulk glassy alloys by controlling the deformation structure, because there are no data on Charpy impact fracture value for the cold-rolled alloys.

The aim of this paper is to improve ductility and plasticity of the bulk Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_5$ glassy alloy by cold rolling. To evaluate the ductility and plasticity, the Charpy impact and bend tests were performed using the bulk glassy alloy samples.

2. Experimental Procedure

A Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_5$ alloy was examined in the present study. The master alloy was prepared by arc melting the mixtures of pure Zr, Cu, Al, and Ni elements in an argon atmosphere. The master alloy was completely remelted, and cast into a plate shape copper mold with a thickness of 3 mm, a width of 10 mm and a length of 70 mm using an argon casting apparatus.$^{13}$ The cast sample was cold-rolled with small reduction ratios of 0.1 to 0.5% per pass. Samples were preformed in various thicknesses to maintain a constant thickness after cold rolling. The cold-rolled samples were covered with MoS$_2$ paste grease to avoid fracture. An Instron test machine was used for the bend test. The sample was 40 mm long, 4 mm wide and 1 mm thick. The support span and cross head
speed in the bend test were 20 mm and 0.0027 mm/s, respectively. The Charpy impact test was performed using a special sample with a size of 55 mm long, 10 mm wide, 2 mm thick and U-notched to 2 mm depth. The structure was examined by optical microscopy (OM) and scanning electron microscopy (SEM).

3. Results and Discussion

3.1 Cold rolling

A number of slip bands were homogeneously introduced by cold rolling, and the cold-rolled samples were divided into numerous small blocks by slip bands. In the reduction ratio range from 0 to 30%, the outline of the slip bands became distinct with increasing reduction ratio, whereas the density of the slip bands was unchanged. Figure 1 shows the SEM images of a side view of the bulk glassy samples, which were rolled to reduction ratios of 10% (a), 20% (b), 30% (c), 40% (d), 50% (e), 60% (f) and 70% (g). The rolling direction is denoted with an arrow in the figure. Initially, the slip bands are formed along the maximum shear stress plane and the angle between the slip bands and the rolled surface is about 45°. This angle is called as “angle θ” in this paper. The slip band density increases at the reduction ratios of a few%, 30% and 60%, accompanying a decrease in angle θ. At 30% reduction ratio, the second slip bands were formed at the angle θ of about 45°. This value agrees with that of the first slip bands as shown in Fig. 1(a). After the introduction of the second slip bands, cold rolling was carried out by the combination between the first and second slip band movements. Some operable slip band marks were accompanied by cracks. The cracks were caused by the mismatch displacement between the first and second slip band systems. The third slip band system is introduced at the reduction ratio value of 60%. Figures 1(f) and (g) show the cold-rolled structure where the first, second and third slip band systems were introduced. The cold-rolled bulk glassy sample is divided into numerous small blocks by such zones, but the sample as a whole has not undergone homogeneous deformation. Therefore, the structure of bulk glassy samples can be controlled by the cold rolling. The cold rolled structure is formed by two regions; deformed (slip band) and undeformed (block) regions.

To distinguish the slip band mark from crack, microscopic observation was performed on the cold-rolled surface using an AFM apparatus. Figures 2(a) and (b) show AFM images of the side surface and edge parts of the 20% cold-rolled sample, respectively. The side surface is shear-deformed plane by the rolling, and the edge is edge part between the rolled plane and side surface. In the figure (a), the region denoted by arrow mark “a” shows the protruding wedge shape region, which was formed by the pseudo-melting in the slip band region. In addition, the edge AFM image in Fig. 2(b) shows the slip steps (marked with “b”, “c” and “d”) without crack. Accordingly, from the microscopic slip band observation, no crack was observed even in the slip band region at the edge part, and the shape of slip band was recognized by the pseudo-melting phenomenon. Furthermore, the much higher reduction ratio causes the generation of the second and third slip band systems, whereas the cross points act probably as an initiation site for cracking in the slip band. The large curvature of slip band also appears to be an originated site for crack formation in the reduction ratio over 30%. However, most of cracks in the slip bands were limited to the surface region, because these fractures were removed by mechanical polishing. Figure 3 shows the fractured regions on the slip bands and the depth dependence of the fractured region of the 60% cold-rolled sample. A visible slip band indicates the existence of step, wedge or crack on the surface, and most of the slip-band marking disappears by careful mechanical polishing to 0.4 μm-depth. All fractured marks in the slip bands perfectly disappeared by 30μm-depth polishing (not shown). Consequently, the distinct crack marks around the intersection of the first, second and third slip band systems were apparent only near the surface fracture sites.

In order to understand the feature of the cold-rolled structure, we summarize the relationship between the reduction ratio and the slip density of the first, second and third slip band systems as shown in Fig. 4(a). After the first slip band system is introduced, the angle θ decreases, and no other slip bands are seen below the next critical point at the 30% reduction ratio. The critical point was defined by the angle θ, which was determined by the balance between the decomposed shear stress of the slant slip band and the threshold shear stress of the new slip band formation. Since the introduction of the slip bands was decided in the limited stress and strain conditions, the angle θ decreases with increasing reduction ratio. Figure 4(b) shows the relationship between the angle θ and the reduction ratio of several slip band systems. Each slip
band system shows a linear relationship between the angle $\theta$ and the reduction ratio. The introduced slip bands can operate in the wide reduction ratio until the angle $\theta$ reaches $0^\circ$. At the critical point of new slip bands, it is also apparent that the angle $\theta$ of the former active slip bands is about $30^\circ$. The worksoftening effect can be estimated by the $\theta$ value, because the value defined by the decomposed shear stress along the slant slip band. The stress value to operate the pre-introduced slip band is about 75% of the threshold stress for the formation of the new slip bands. This plastic deformation mechanism brings about the peculiar cold-rolled structure, which is similar to tensile deformation of a single crystal. Their structures
are similar each other on the view points of perfect homogeneous structure and continuous elastic materials, though the yield strength of a single crystal is much lower than that of the bulk glassy alloy.

3.2 Bend test
To clarify the "work softening" phenomenon of the cold-rolled bulk glassy alloy, we observed the re-operation behavior of slip bands on the surface during the bend test. Since the cold-rolled samples for bend test were pre-formed to one size and polished like a mirror, micro Vickers indenter marks were put on the surface to determine the position of the slip-band marks caused by cold rolling. The determination of the same slip band re-operation during the bend test can be achieved by confirmation of position from the micro Vickers indenter marks. In the bend test, the rolling direction is along to the longitudinal direction of the samples, because the operation of slip bands relaxes tensile strain at the surface of the bending sample. Figure 5 shows the changes in the side surface structure; (a) the 20% rolled sample, (b) after polishing, (c), (d) bending in different deflections, and (e) after bending-fracture. A notable point in this figure is the re-operation of slip bands during the bend test. The distinct re-operated slip band marks were identified with I to IV roman numbers. The visible slip band marks during bending test can be recognized as pre-introduced slip bands by cold rolling.

During the bending test, a few of reloading processes have been tried to reveal that the slip band is not accompanied by crack. Figure 6 shows the bend load versus bend deflection curves of the same sample in Fig. 5, and (c), (d) and (e) are marked to show each condition of the sample in Figs. 5(c), (d) and (e), respectively. In the Fig. 6, bending stress is defined following equation; \[ \sigma = \frac{3FL}{2bh^2} \], where \( P \) is the bending load, \( f \) is the support span, \( d \) and \( h \) are the width and thickness of the sample. The movement of each pre-introduced slip band can release the applied bending strain by partial yielding, which is recognized by the existence of significantly increased bend deflection. However, no clear slip-band marks are observed in the apparent elastic zone, which is recognized in the net linear relation between the bend load vs. bend deflection stage. A number of pre-introduced slip bands can move within small distance in the transition stage from elastic to plastic deformation. Therefore, slip band marks are too small to detect by SEM. In the apparent elastic zone, the gradient of the bend load vs. bend deflection curve is related to Young’s modulus. Since the atomic structural change does not occur by such a small strain of bend test, the Young’s modulus is not changed by bend deflection. The decrease in the gradient just before fracture in (d) means a decrease of the net cross sectional area by partial failure on the slip bands. In this case, it is estimated that the decrease ratio of effective cross-sectional area is about 3.5% from the decrease in Young’s modulus from 85 to 82 GPa.

Furthermore, the slip bands on the surface are slightly curved, implying the displacement limit of each slip band. Takeuchi and Maeda reported\(^{(4)}\) that the curve of the slip bands in the bulk glassy alloy was an intrinsic phenomenon, which could be reproduced by computer simulation. The curvature of the slip band was a significant factor to evaluate the strength and ductility, because the enormous displacement on the slip bands brings about many cracks by mismatching among curved slip bands. As described above, the control of slip band structure in the density and homogeneity was the most important factor to improve ductility and plasticity by the cold rolling.

To estimate the improvement of bend plasticity caused by cold rolling, bend load vs. bend deflection curves of the cold-rolled samples with different reduction ratios are shown in Fig. 7. The bend deflection increases significantly with increasing reduction ratio. A slight decrease in the maximum bend load is also observed for the samples with higher reduction ratios. The bend load mainly depends on the bend moment, but the decrease in the maximum bend load is caused by the extent of partial yielding at the pre-introduced slip bands near the surface. However, the bend deflection is an important factor to estimate plasticity in the bend test. Accordingly, the significant increase of the bend deflection is due to the change in the cold-rolled structure with reduction ratio, e.g. density and homogeneity of slip bands. Side surface structure of the bent samples with different reduction ratios was also observed using an optical microscope. Figure 8 shows the side surface view of the bent sample without cold rolling. The bend deflection was about 2 mm. Substantially deformed slip-band marks are mainly observed around the loading point as shown in Fig. 8(a). Many cracks in the slip bands are also observed around the loading point as shown in Fig. 8(c). Figure 9 shows the side surface view of the bent sample with a reduction ratio of 20%, which is subjected to the same deflection of about 2 mm. In Fig. 9(a), no distinct slip-band marks are observed in the side view of the sample. Microscopic obser-
Fig. 5 SEM images of slip bands introduced by cold rolling (a), after polishing to rub off the slip bands' marks (b) and the slip bands' formation during the bend test (c) to (e). The roman numerals indicate the correspondence between the slip bands in cold-rolled and bend test states.

Fig. 6 Bend load vs. bend deflection curve of the 20% cold-rolled alloy.

Fig. 7 Bend load vs. bend deflection curves of the cold-rolled bulk glassy alloys with reduction ratios of 10%, 20%, 30%, 40%, 50%, 60% and 70%.

...was also performed to evaluate the movement of operable slip bands in the bend strain state. Figure 9(c) shows the magnified images of the surface edge regions in the sample. These images show fine homogeneous slip-band marks growing from surface to inside along the maximum shear stress plane.

Consequently, by the constructive surface observation of...
the two bent samples with reduction ratios of 0 and 20\%, it is summarized that the fine structure of pre-introduced slip bands releases the bend strain homogeneously, and eliminates localized strain around the loading point as shown in Fig. 8(c). The cold-rolled structure indicates that the bend plasticity can be enhanced by the work-softening phenomenon resulting from a number of pre-introduced slip bands.

3.3 Charpy impact test

It is generally known that crack propagation is caused by partial yielding at the crack tip to release the pile-upped local elastic strain. The local yielding in the bulk glassy alloy also causes crack propagation. Since the local yielding region is composed of many operable slip bands in the pseudo-melting state, the fracture stress must be sensitive to strain rate.\textsuperscript{13) }In the case of large strain rate, the yield strength of plastic deformation decreases. Therefore, the Charpy impact test is the most severe test to estimate the ductility of bulk glassy alloy. We prepared the Charpy impact test samples with a size of 10 mm in width, 55 mm in length and 2 mm in thickness. The ductility of cast bulk amorphous alloy closely depends on the thickness, the thinner one shows good ductility and the thicker one shows brittle. The thickness was determined experimentally, because the upper limit thickness of the cast sample with sufficient ductility was estimated to be about 2.5 mm. The cast samples were rolled to the reduction ratio of 20% to estimate the improvement of ductility by cold rolling.

The fractured surface after the Charpy impact test mainly consisted of three different regions: (1) a vein pattern in a plane strain state, marked with vein I, (2) a vein pattern in a plane stress state, marked with vein II, and (3) brittle fractured crystalline areas, as shown in Fig. 10. In this figure (a), a most of the fractured area is occupied by vein I, which includes a small colony of crystalline particles, a few micrometers in diameter, for the samples that are not rolled. The vein II area is seen in the circumference of the fractured surface, and the region is considered in a plane stress state. For ordinary crystalline alloys, a decrease in Charpy impact energy depends on the ratio of the brittle fractured surface area, because the Charpy energy is regarded as the formation energy of the fractured surface. In our study, the brittle fractured surface is a crystallized area, which can be controlled by cooling rate during casting. The finally, completely crystallized samples are prepared by full annealing at the temperature just above the crystallization temperature for 360 ks. Figure 11 shows the relationship between the Charpy impact value and the crystallized area ratio in the fractured surface, and the relationship seems to have linearity. The deviation of the 39% crystallized sample from this line is probably caused by the

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Fig. 8 Bending side view of the no-rolled glassy alloy (a), schematic illustration of the same bending glassy alloy (b) and magnified OM images in the I, II, III regions as shown in (b).
difficulty of detecting small crystallized areas. The Charpy impact value of the bulk glassy sample without crystalline phase is about 178 kJ/m². The present Charpy impact value is not a net value, because the size of the sample does not satisfy the ASTM and JIS standards. However, the fractured surface was composed mainly of one flat surface with vein I pattern. To determine the size effect on the Charpy impact value, preliminary experiments were performed using ductile cast iron samples with different thicknesses. As a result, the Charpy impact value of the 2 mm thick sample was about 1.33 times larger than that for the samples of 10 mm thickness in regular JIS (not shown).

The enhancement effect of ductility by rolling was examined using two samples with different rolling directions; rolling direction parallel to the impact direction, marked with∥, and rolling direction perpendicular to the impact direction, marked with⊥. The 20% rolled∥ sample shows equal value against the as-cast samples. Besides, the 20% rolled⊥ sample shows a significant increase of the Charpy impact value by about 36%. This fact indicates that the ductility of the bulk glassy alloy can be improved by cold rolling. To clarify the mechanism for the improvement of ductility, three samples' fractured surfaces were observed; no-rolled, 20% rolled∥, and 20% rolled⊥. Figure 12 shows the matching SEM images of the fractured surface of the as-cast sample. In this paper, matching photographs will be paired, if the figure bends along the boundary between the matching photographs. The fractured surface is characterized by the pronounced vein I pattern, which is similar to the dimple mark of the fracture mode I. Figure 13 shows the matching SEM images of the fractured surface of the 20% rolled∥ sample. The fractured surface is composed mainly of one slipped plane, which is similar to the tensile fractured surface. In the microscopic observation, the fractured surface is rugged on a scale of a few micrometers. The fractured surface was slanted by about 45° towards the free surface of the sample. The fractured sample does not satisfy the mode I, whereas the Charpy impact value is equal to that of the as-cast sample. Figure 14 shows the matching SEM images (a,b) and the matching topographic images (c,d) of the 20% rolled⊥ sample. Only in this figure, pre-introduced slip-band marks are clearly seen in these images, and the slip-band marks are seen in the entire fractured surface with the vein I pattern. The slip-band marks in these images are slanted by about 45° against the crack propagation direction, which is marked with a large arrow. Furthermore, the existence of enlarged slip band marks in the fractured surface points out that the superior operation of the slip bands occurred by the Charpy impact crack propagation. The introduced slip bands re-operation cause resistance of the crack.
propagation. In generally, the Charpy impact crack propagation needs the energy of fracture surface making as shown in Figs. 12 and 13. However, in Fig. 14, the Charpy impact crack propagation needs excess energy to operate pre-introduced slip bands that can be guessed from pronounced pre-introduced slip band marks on the fractured surface.

Consequently, in the slip band, the pseudo-melting state was probably enhanced by the impact fracture. These slip bands acted to resist the crack propagation, because the superior deformability of the slip bands can be released elastic stress field at the crack tip. Therefore, in the amorphous sample, determination of rolling direction is the important factor to enhance ductility by cold rolling. That is to say, slip bands should be introduced in the sample to across the crack propagation passage.

4. Summary

Utilizing the “work softening” phenomenon of the Zr-based bulk glassy alloy, we have attempted to improve ductility by cold rolling. The problem of ductility improvement is originated from the unique feature of deformation mechanism caused by work softening. The critical stress for the sample subjected to slip deformation is smaller than that for the no-slipped sample. Therefore, the introduction of a high density of operable slip bands is favorable for the appearance in uniform deformation. For the bulk glassy alloy with high strength and without significant macroscopic elongation, the existence of a uniform deformability is expected to bring about an increase in ductility. The results obtained are summarized as follows.

1) In the cold rolled structure, the density of slip band suddenly increased at three step modes at each reduction ratios of a few, 30 and 60%.
Fig. 12 Matching SEM images of the Charpy impact fractured surface in the non-rolled sample.

Fig. 13 Matching SEM images of the Charpy impact fractured surface in the 20% rolled \parallel sample.

Fig. 14 Matching SEM images ((a) and (b)) and topographic images ((c) and (d)) of the Charpy impact fractured surface in the 20% rolled \perp sample.
(2) By preliminary cold rolling of the bulk glassy alloy, the uniform deformation under bending stress condition increased. The maximum bend deflection increases significantly with increasing reduction ratio.

(3) To enhance ductility for the cold-rolled alloy, slip bands should be introduced along the direction perpendicular to the crack propagation direction. This is due to the effective operation of the preliminary introduced slip bands to release the strain field in front of crack tip.

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