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Plasticity Improvement of Amorphous Alloy via Skim Cold Rolling

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This study reports the plasticity improvement of amorphous alloy associated with skim cold rolling. It was found that, with an increasing reduction in thickness of up to 6 %, the plastic strain increased considerably from 1.5 % to 9.6% while the yield strength deceased slightly from 1.75 GPa to 1.68 GPa. With further rolling beyond 6 %, the changes in the plasticity and yield strength were observed to be insignificant. In this study, we discussed the principle underlying the improved plasticity of amorphous alloy in view of the creation of excess free volume during skim cold rolling.

Keywords: amorphous alloy, excess free volume, nanocrystals, chemical heterogeneity, plasticity

1. INTRODUCTION

It is well known that the global plasticity of amorphous alloys is achieved by the formation of shear bands. Therefore, improving the plasticity is a matter of generating a large number of shear bands. In general, shear bands form at local heterogeneities in amorphous alloys [1,2]. Nanocrystals, chemical heterogeneities, and excess free volume are the typical examples of these heterogeneities and can be generated under various stress states subjected to amorphous alloys. According to thermodynamics, hydrostatic compression promotes amorphous-to-crystalline phase transformation [3]. Meanwhile, shear stress imposed on amorphous alloys can induce the formation of excess free volume [4]. The fact that nanocrystals, chemical heterogeneities, and excess free volume are formed by the application of stress [3,5,6] suggests that mechanical working can be a potential technique to enhance the plasticity of amorphous alloys.

Rolling, equal channel angular pressing, compressive preloading, etc. were reported to be efficient in improving the plasticity of amorphous alloys [7,8,9,10]. Of these techniques, cold rolling demonstrates feasibility for practical application in view of its ability to effectively introduce the structural heterogeneities and easily control the stress state by adjusting the reduction ratio. Such characteristics of rolling promote the formation of various heterogeneities, including nanocrystals, chemical heterogeneities, and excess free volume, which in turn contribute to the improvement of the plasticity by facilitating the formation of multiple shear bands while retarding their propagation [7,8].

Many studies have reported that cold rolling is an effective technique for enhancing the plasticity of amorphous alloys. However, most research on cold rolling reported to date has used a high degree of plastic deformation [5,6,7,8], which sometimes causes the premature failure of the workpiece. It is believed that excess free volume can be generated even during earlier stages of deformation or under a stress lower than the global yield strength [11,12]. Therefore, skim cold rolling with a low degree of reduction can be an alternative route that is not only effective in improving the plasticity, but also preventing the premature failure of the workpiece during rolling.

We investigate the change in the plasticity of a Zr-based amorphous alloy associated with skim cold rolling. The microstructural changes of the rolled samples were examined in order to understand the dominant factors responsible for the change in the mechanical properties. Based on the experimental observations, we proposed the concept of a post-treatment technique that can improve the plasticity of amorphous alloys while preventing the formation of premature cracks.

2. EXPERIMENTAL PROCEDURES

Ingots with a nominal composition of $Zr_{57}Cu_{20}Al_{10}Ni_8Ti_5$

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(in at.%) were prepared by arc melting mixtures of Zr (99.7 %), Cu (99.9 %), Al (99.9 %), Ni (99.9 %), Ti (99.9 %) under a purified Ar atmosphere. Each ingot was remelted several times to ensure microstructural homogeneity and then cast into a copper mold to produce a 40 mm long rectangular plate with a thickness and width of 1.5 mm and 8 mm, respectively. The as-cast sample was then rolled by a twin roll (diameter of 10 cm) with a constant perimetric speed of about 2 mm/s. The deformation degree was denoted by the reduction in thickness, i.e., $R = (t_0 - t)/t_0$, where t_0 and t represent the specimen thickness before and after rolling, respectively. Cold rolling was conducted unidirectionally to various final reductions (up to~11 %) with a 0.5 % reduction per passage.

The rolled samples were machined to the rectangular rods with a dimension of 1.5 × 1.5 mm^2 in the cross-section and 3 mm in height and were tested in compression at a strain rate of 1×10^{-4} s^{-1} at room temperature. The changes in the excess free volume associated with rolling were measured using differential scanning calorimetry (DSC, Perkin-Elmer DSC 7, USA) at a heating rate of 40 K/min. Microstructural analysis was carried out using an analytical high resolution transmission electron microscopy (HRTEM, FEI TECNAI G^2 F-20, 200 keV, The Netherlands). The TEM samples were perforated by electro-chemical jet thinning using a 20 vol.% solution of nitric acid in methanol at –40 °C.

3. RESULTS AND DISCUSSION

Figure 1(a) exhibits the engineering stress-strain curves recorded from the as-cast sample and the samples subjected to different reduction ratios, showing how the flow behaviors vary with increasing reduction ratio. The plasticity improvement of the amorphous alloy is quantitatively measured and shown in Fig. 1(b). As can be seen in Figs. 1(a) and (b), by increasing the reduction up to 6%, the plastic strain increased considerably from 1.5 to 9.6% while the yield strength slightly decreased from 1.75 GPa to 1.68 GPa. With further rolling beyond 6 %, the change in the plasticity and yield strength were observed to be insignificant.

In general, bulk amorphous alloys fail due to the formation of shear bands. Since the plastic deformation achieved by bulk amorphous alloys is virtually confined at narrow regions near shear bands, the extent of the plastic deformation in bulk amorphous alloys is largely dependent on the number density of the shear band. Therefore, it is expected that the samples considered in this study will differ both in the number density and the shape of the shear bands. Presented in Fig. 2 are the SEM micrographs recorded from the side surfaces of the fractured as-cast and rolled samples, showing completely different patterns of the shear band formation. Major differences can be found from the number densities of the shear bands, band length, and band shape; in

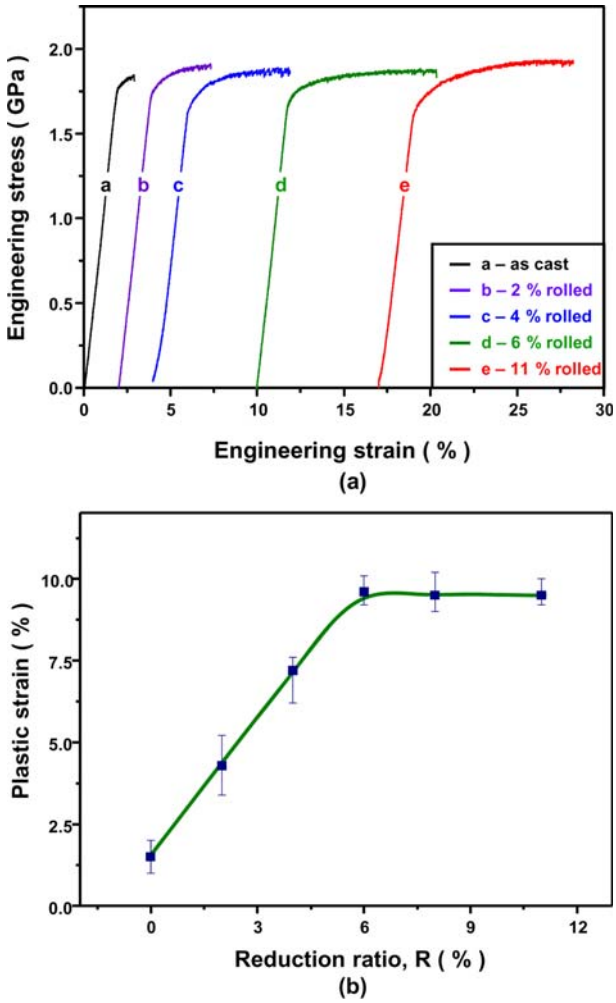

Fig. 1. (a) Compressive stress-strain curves obtained from the as-cast sample and the samples rolled to different reduction ratios and (b) Variations in the plastic strain of the samples as a function of the reduction ratio.

the case of the as-cast sample, negligible numbers of shear bands were observed, while a number of tortuous shear bands developed over the entire length of the samples subjected to rolling to more than 6 %. Considering that the mechanical properties of amorphous alloys are intimately related to the amount of structural heterogeneities, including nanocrystals, chemical heterogeneities, and free volume, it is necessary to examine the structural changes at the early stage of cold rolling in order to explain the improvement of plasticity during skim cold rolling.

It is reported that cold rolling promotes the formation of various heterogeneities, including nanocrystals, chemical heterogeneities, and excess free volume, which in turn affect the mechanical properties. Therefore, the samples were first observed using HRTEM to confirm if there were structural changes caused by cold rolling. Two samples, i.e., the as-cast one and the one rolled to an 8 % reduction, were selected as

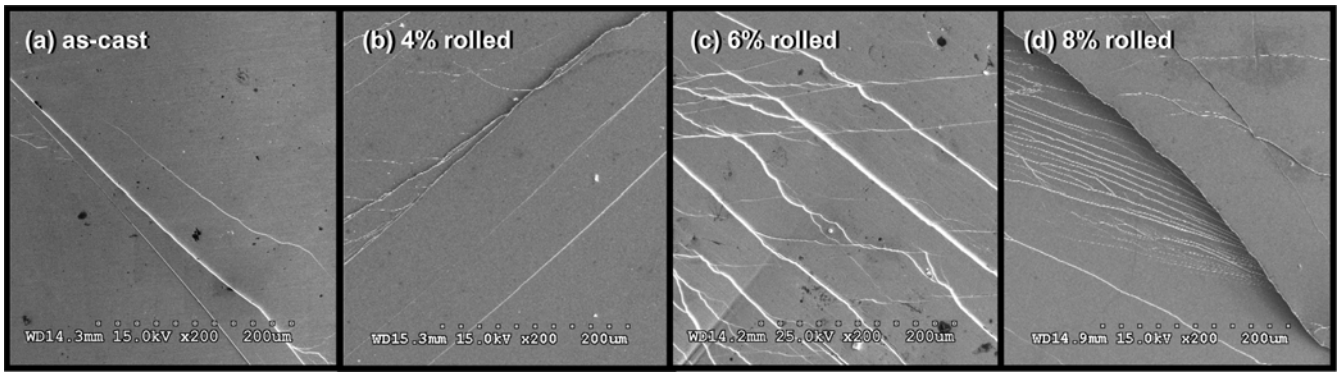

Fig. 2. SEM micrographs recorded from the side surfaces of the fractured samples: (a) as-cast, (b) 4 % rolled, (c) 6 % rolled, and (d) 8 % rolled samples.

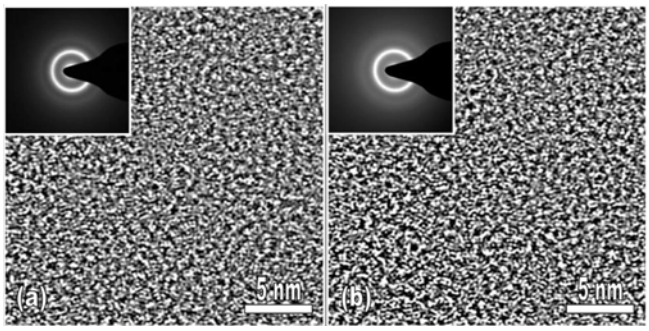

Fig. 3. HRTEM images of (a) the as-cast and (b) the rolled sample with the reduction ratio of 8 %, showing both samples to be fully amorphous.

the representative samples. Figure 3(a) shows the HRTEM image obtained from the as-cast sample, showing a fully amorphous structure without any lattice fringe. The halo diffraction ring in the selected area diffraction pattern (SADP) corresponding to the HR image further confirms its amorphous nature. Figure 3(b) shows the HRTEM image along with the corresponding SADP of the sample rolled to 8%, revealing a fully amorphous nature without any evidence of the presence of nanocrystals. This was again confirmed by measuring the crystallization enthalpies of the rolled samples. As can be seen from Fig. 4, even with a slight decrease in the crystallization enthalpy, its change within the reduction ratio used in this study was insignificant. Therefore, judging from the TEM and DSC results, the possibility of crystallization in the early stage of deformation during rolling can be ignored, and, thus, its effect on the plasticity would be negligible.

It is known that the chemical heterogeneities formed as a result of the phase separation during casting can also improve the plasticity of amorphous alloys [13]. These heterogeneities can also be formed during rolling [5]. Therefore, this study examined if skim rolling induces the chemical heterogeneity formed as a result of phase separation. As can be seen in Fig. 3(b), no contrast difference in the HR image was

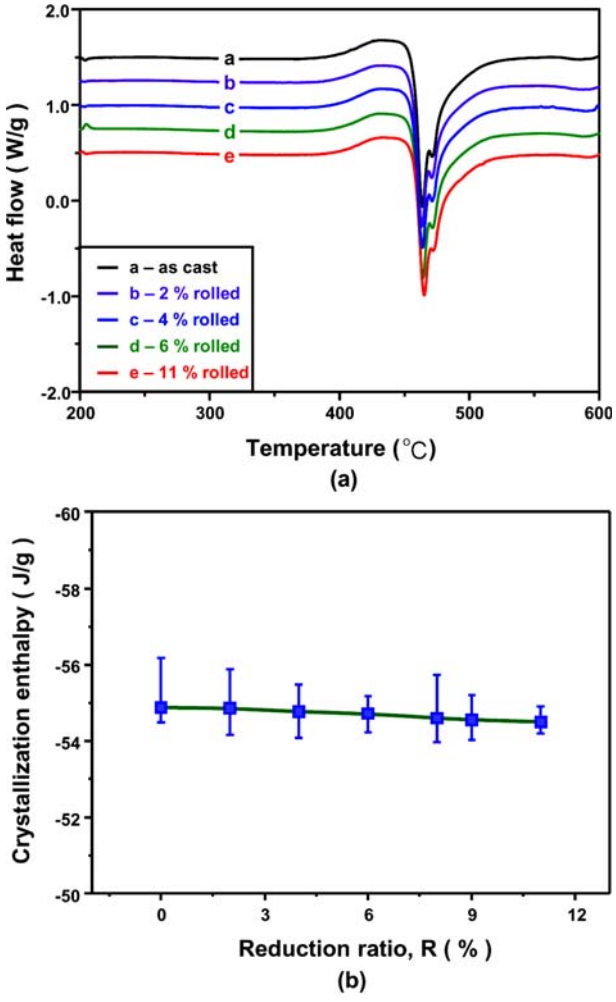

Fig. 4. (a) DSC thermograms of the as-cast sample and rolled samples and (b) Variation in the crystallization enthalpy measured from the as-cast and rolled samples, showing that the enthalpy values are almost the same within the measurement error. The symbol is the average of five measurements.

observed from the rolled sample, indicating that the phase separation in the atomic-scale did not occur. However, it is

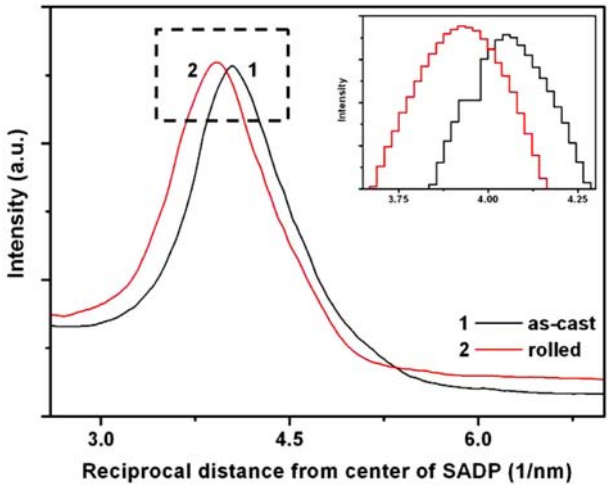

Fig. 5. Average intensity profile of the selected electron diffraction pattern measured from the as-cast and the rolled sample with a reduction ratio of 8 %. Note that the peak positions of the SADPs are the average of ten measurements, which are the distances from their center to the highest intensity positions along the radial direction.

necessary to further examine in detail whether or not atomic-scale phase separation exists. Considering that the average interatomic spacing of the chemical heterogeneity is different from that of the matrix of the sample, their reciprocal lattice distances are also different. Therefore, the presence of the chemical heterogeneity was confirmed in this study by observing the splitting intensity profile of the SADP recorded from the rolled sample. However, as can be seen in Fig. 5, the peak of the SADP recorded from the sample rolled to 8 % was not split, suggesting again that skim rolling did not induce any phase separation or crystallization.

In the mean time, Zhang et al., from the rolling experiment of a Zr-based alloy similar in composition to the one used in this study, reported that chemical heterogeneities and nanocrystals were observed from samples only when they were reduced by more than 90 % in thickness [14]. The earlier study suggests that, in order to mechanically induce phase separation and crystallization, it is necessary to supply a high degree of mechanical energy, which indirectly confirms why the present sample did not show any evidence of the formation of chemical heterogeneities and nanocrystals in the skim rolled samples.

In general, both phase separation and crystallization are accompanied by long-range diffusion, which normally requires energies high enough for the phase transformation to take place. In contrast, excess free volume can be formed readily even under the application of low mechanical energy. In fact, we experimentally demonstrated that excess free volume can be formed at a stress level much smaller than the global yield stress [11,12], affecting the mechanical and physical properties of amorphous alloys. In addition, through a combination of experiments and simulations, Park *et al*. [15] showed that amorphous alloys with a larger excess free volume had lower strength and higher plasticity, which again was confirmed by Huang *et al*. [16]. As such, it would be more appropriate to explain the changes in the flow behaviors based on excess free volume.

It is noted from Fig. 5 that the average radius of the SADP recorded from the rolled sample was slightly smaller than that of the as-cast one. Since the radius of the SADP is a distance in the reciprocal space, the reduced reciprocal distance of the rolled sample corresponds to the increased average atomic spacing. This increased atomic spacing is probably due to the generation of the excess free volume associated with skim cold rolling. Accordingly, the measurement of the relative excess free volume is needed to clearly explain the type of structural changes that occurred during rolling and its measurement can, therefore, provide information on the variation in the mechanical properties as a result of skim cold rolling.

Since the amount of excess free volume is proportional to the energy release associated with the structural relaxation (or the annihilation of excess free volume) during heating below the glass transition temperature [17], the amount of heat release measured from DSC reflects the amount of '*relative*' excess free volume. Therefore, DSC can be used as a practical means of measuring the relative amount of excess free volume. Figure 6(a) shows the DSC thermogram of the as-cast sample, which was compared with those of the cold-rolled ones. The regions below the glass transition temperature were superimposed on the same graphs in the inset of Fig. 6(a) to show the variations in the exothermic heat associated with the structural relaxation of the samples. The result showed that the amount of the exothermic heat increases considerably after skim cold rolling. This experimental observation provides direct evidence that skim cold rolling did indeed create excess free volume. The variation of the exothermic heat is also shown as a function of the reduction ratio and shown in Fig. 6(b) in order to demonstrate how excess free volume changes with the reduction ratio. The result indicates that excess free volume increased with the increasing reduction ratio and reached the maximum at the reduction ratio of 6 % followed by a gradual decrease upon further rolling.

The varying tendency in the free volume in Fig. 6(b), as quantitatively determined by measuring the exothermic heat, is considered to stem from the competitive role played by the generation process and annihilation process of excess free volume [4]. At the earlier stage of cold rolling, the generation rate of free volume is dominant, resulting in an increase in free volume. Upon further rolling, the amount of excess free volume increases, causing the amorphous alloy to possess a higher energy state. As such, the alloy tends to lower its free energy by annihilating excess free volume. At this stage, the generation rate is considered equal to annihilation

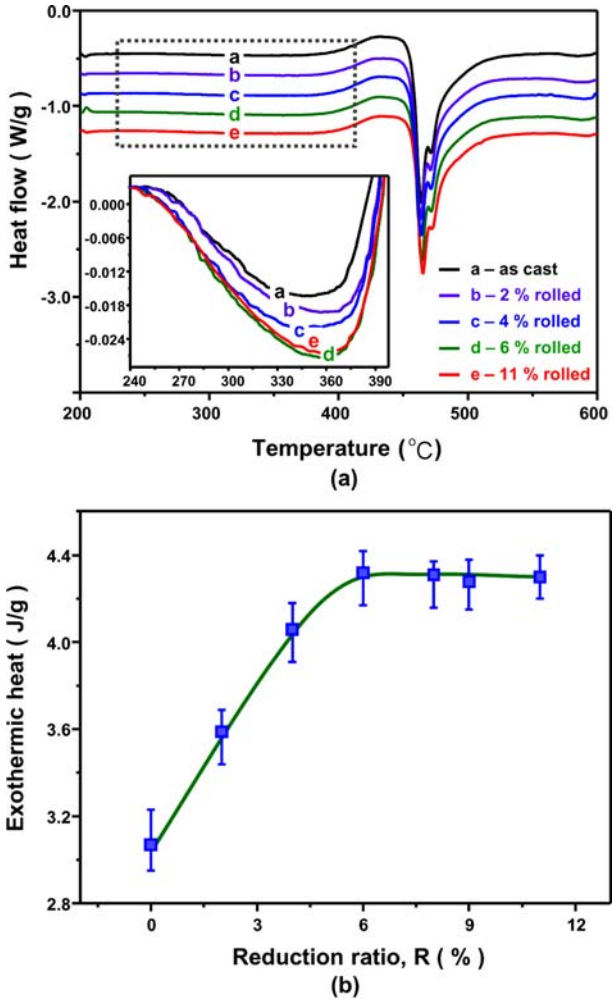

Fig. 6. (a) DSC thermograms recorded from the as-cast and rolled samples with different reduction ratios and (b) Variation in the exothermic heat of the rolled samples measured as a function of the reduction ratio.

rate and the equilibrium state is established, leading to the saturation of the excess free volume. In the meantime, Wright *et al.* [18] claimed that, after reaching a critical amount, excess free volume is annihilated by forming more stable voids. Some recent studies also confirmed the presence of voids, which are believed to be formed by the coalescence of excess free volume in the severely rolled samples [19,20]. Therefore, although further validation experiments have to be performed in the future, the aforementioned discussions explain why the amount of excess free volume tended to saturate upon further rolling exceeding the reduction ratio of 6 %.

Since the mechanical and physical properties of amorphous alloys are closely related to the amount of excess free volume, the variation of mechanical properties can be explained based on the change in excess free volume. Considering that the local rearrangement of atoms in amorphous alloys is promoted by the applied stress under the presence of abundant free volume, the enhanced plasticity of the rolled samples is thought to be due to excess free volume generated during skim cold rolling. In addition, abundant free volume in amorphous alloys causes an increase in the average interatomic spacing, which not only reduces the atomic bonding strength, but also causes the atoms to flow at a lower stress level. As such, a slight decrease in the yield strength of the rolled samples as in Fig. 1(a) is also due to the formation of free volume associated with rolling.

4. CONCLUSIONS

According to the cold rolling experiment conducted on a monolithic amorphous alloy, the following conclusions were drawn.

1. With increasing reduction in thickness up to 6 %, the plastic strain increased considerably from 1.5 % to 9.6 %, while the yield strength deceased slightly from 1.75 GPa to 1.68 GPa. With further rolling beyond 6 %, the changes in the plasticity and yield strength were observed to be insignificant.

2. Skim cold rolling did not induce heterogeneities including phase separation and crystallization. However, a considerable amount of excess free volume was observed to exist in the rolled alloy as evaluated by the exothermic heat measured by DSC, which in turn altered the mechanical properties.

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