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## Free-volume evolution and its temperature dependence during rolling of $\text{Cu}_{60}\text{Zr}_{20}\text{Ti}_{20}$ bulk metallic glass

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The free-volume evolution during rolling  $\text{Cu}_{60}\text{Zr}_{20}\text{Ti}_{20}$  bulk metallic glass at room and cryogenic temperatures has been investigated by differential scanning calorimetry. When the specimen is rolled at cryogenic temperature, the free-volume content increases as the rolling proceeds first, and then saturates accompanied by the occurrence of phase separation as the thickness reduction exceeds 89%. If the rolling is performed at room temperature, although the free-volume content also rises in the earlier stage, it tends to decrease rather than saturate when the thickness reduction exceeds 87%, accompanied by partial crystallization. Phase separation does not change the annihilation rate of free volume, while the appearance of crystal/amorphous boundaries can enhance the annihilation.

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Plastic deformation of crystalline materials is realized by multiplication and glide of dislocations. The dislocation tangle and pile-up in the deformed areas induce work hardening, which promotes other areas to deform. Therefore all the volume elements in such materials contribute to the plastic deformation. Different from crystalline materials, metallic glasses lack the long-range translational symmetry in the atomic assembly, and have no well-defined atomic planes or slip systems.<sup>1</sup> Their deformation no longer complies with the dislocation theory, but occurs as a result of a number of individual atomic jumps.<sup>2</sup> Plastic deformation of metallic glasses has two modes.<sup>2,3</sup> At high temperatures and low stresses, a homogeneous flow occurs, but at low temperatures and high stresses, the deformation exhibits an extreme inhomogeneity, i.e., the plastic strain is localized in the shear bands. Although adiabatic heating, which can bring about the viscosity reduction in the shear bands, was ever argued to be responsible for the deformation,<sup>4</sup> there has been more and more evidence to indicate the dominative role of generation in the deformation mechanism.<sup>5</sup>

Theoretical analyses have pointed out that whether the deformation is homogeneous or inhomogeneous, the free-volume content in a metallic glass increases as the plastic deformation proceeds, and saturates when the strain exceeds a certain value.<sup>6-8</sup> This phenomenon has been observed in the homogeneous tensile deformation of  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$  glass ribbon at high temperature, where the ribbon remained amorphous after the content was saturated.<sup>9</sup> Decreasing the deformation temperature in a certain range brought about the rise of the saturated free-volume content. At temperatures far below the glass transition, as metallic glasses exhibit little global plasticity under uniaxial tension before catastrophic frac-

ture occurs along a narrow shear band,<sup>4</sup> it is impossible to detect the saturation of free-volume content in the tensile deformation. At the same time, limited by the sample size, the actual deformation degree achieved in the compressive deformation of metallic glass ribbons was not too high, where the free-volume content was found to always increase with the deformation.<sup>10</sup> Therefore, the saturation of free-volume content under inhomogeneous low-temperature deformation still needs to be experimentally verified. The discovery of bulk metallic glasses (BMGs) makes it possible to obtain a high degree of deformation under compressive deformation.<sup>11</sup> In the present work, we rolled the  $\text{Cu}_{60}\text{Zr}_{20}\text{Ti}_{20}$  BMG to a very high strain level at room temperature (RT) and cryogenic temperature (CT), respectively, and the saturation of content has been observed.

$\text{Cu}_{60}\text{Zr}_{20}\text{Ti}_{20}$  cylindrical rods with a diameter of 2 mm and a length of 40 mm were obtained by suction casting into a copper mold. The amorphous structure was ascertained by x-ray diffraction with monochromatic  $\text{Cu } K\alpha$  radiation and transmission electron microscopy (TEM). The rods were cut into short cylinders with a thickness of 1.5 mm for rolling. The detailed procedure for rolling deformation has been described elsewhere.<sup>12</sup> A continuous liquid-nitrogen stream was used to cool the specimen throughout the CT-rolling operation, and the temperature of the specimen was measured to be about 150 K. The degree of deformation is denoted by the reduction in thickness  $\epsilon = (h_0 - h)/h_0$ , where  $h_0$  and  $h$  represent the specimen thicknesses before and after rolling, respectively. The strain rate was carefully controlled to be about  $5.0 \times 10^{-3} \text{ s}^{-1}$ . The microstructures of the specimens subjected to different degrees of deformation were examined by JEOL JEM-3000F high-resolution TEM (HRTEM) with an accelerating voltage of 300 kV. The specimens used for the HRTEM experiments were prepared by low-energy ion milling at 2.5 kV and 5 mA with liquid-nitrogen cooling.

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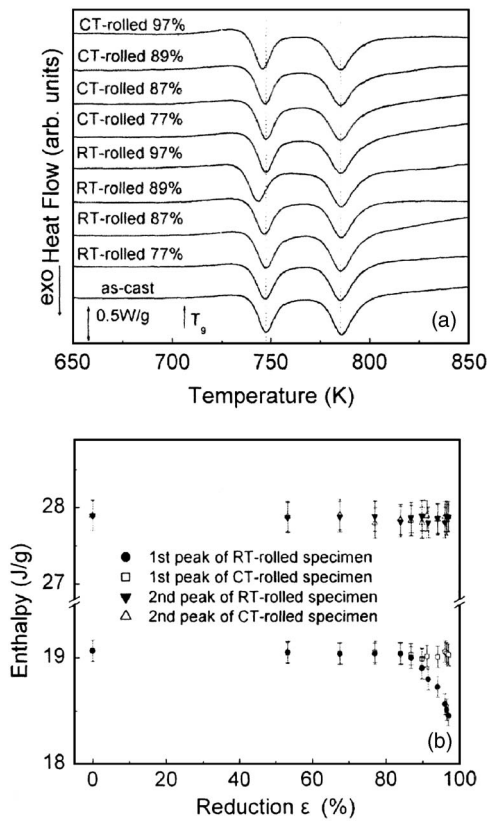


FIG. 1. (a) DSC curves of the RT-rolled and CT-rolled  $\text{Cu}_{60}\text{Zr}_{20}\text{Ti}_{20}$  specimens with different  $\epsilon$  at 20 K/min. (b) The enthalpies of the first and second exothermic events for the RT-rolled and CT-rolled specimens as a function of  $\epsilon$ .

Thermal analyses were performed in a Perkin–Elmer Pyris Diamond differential scanning calorimeter (DSC) at 20 K/min under a flow of purified argon. A second run under identical conditions was used to determine the baseline after each measurement run. The sample and reference pans were made of aluminium. The temperature and the heat flow were calibrated by measuring the melting temperatures and the heats of fusion of pure In, Sn, and Zn.

Thickness reduction as high as 97% was achieved in both rolling deformations at RT and CT. Figure 1(a) shows the DSC curves of the RT-rolled and CT-rolled specimens with different  $\epsilon$  at 20 K/min. The as-cast  $\text{Cu}_{60}\text{Zr}_{20}\text{Ti}_{20}$  specimen exhibits an endothermic event, characterized by a glass transition temperature  $T_g=706$  K, followed by two exothermic events, the first one corresponding to amorphous-to- $\text{Cu}_{51}\text{Zr}_{14}$  phase transition while the second one being due to the crystallization of the residual amorphous phase.<sup>13</sup> Figure 1(b) shows the variations in enthalpy of the first and second exothermic events for the RT-rolled and CT-rolled specimens as a function of  $\epsilon$ . It is evident that the enthalpy of the first exothermic event keeps constant for the RT-rolled specimens when  $\epsilon$  is less than 87%, but then decreases by about 3% from  $\epsilon=87\%$  to  $\epsilon=97\%$ , while that for the CT-rolled specimens remains unchanged at all  $\epsilon$  values. The enthalpy of the second exothermic event does not change with  $\epsilon$  whether the rolling is performed at RT or CT. These experimental results indicate that crystallization is involved in the RT-rolled specimens with  $\epsilon>87\%$ , while in the CT-rolled specimens no mechanically driven crystallization occurs. Figure 2 shows a HRTEM image of the RT-rolled specimen with  $\epsilon=97\%$ . Clear lattice fringes are observed, further confirming

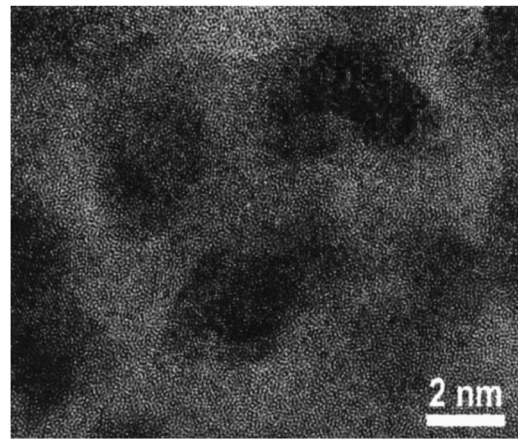


FIG. 2. HRTEM image of the RT-rolled  $\text{Cu}_{60}\text{Zr}_{20}\text{Ti}_{20}$  specimen with  $\epsilon=97\%$ . Visible lattice fringes confirm the existence of nanocrystallites.

that crystallization has occurred in the RT-rolled specimen.

Van den Buekel *et al.*<sup>14</sup> has noted that the change in free-volume content during a constant heating rate DSC experiment is proportional to the energy released by the structural relaxation of metallic glasses. Figures 3(a) and 3(b) present the DSC curves, expressed in the relative change of the apparent specific heat  $\Delta C_p=C_p(T)-C_p(323\text{ K})$ , where  $C_p(323\text{ K})$  and  $C_p(T)$  are the apparent specific heat of specimens at 323 K and temperature  $T$ , respectively. The onset

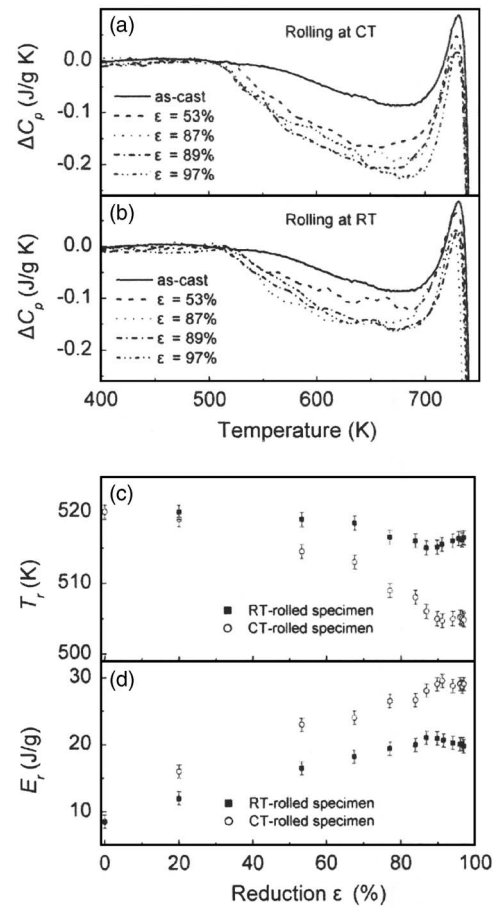


FIG. 3. Specific heat data of the RT-rolled (a) and CT-rolled (b)  $\text{Cu}_{60}\text{Zr}_{20}\text{Ti}_{20}$  specimens with different  $\epsilon$ . The onset temperature,  $T_r$ , of structural relaxation (c) and the released energy per unit mass of amorphous phase,  $E_r$ , during structural relaxation (d) as a function of  $\epsilon$ .

temperature,  $T_r$ , of structural relaxation of the RT-rolled and CT-rolled specimens varies with  $\epsilon$  as shown in Fig. 3(c). It is about 520 K for the as-cast specimen, and monotonously decreases to 515 K as  $\epsilon$  in the RT-rolled specimen increases to 87%. At higher  $\epsilon$ ,  $T_r$  begins to slightly increase. For the CT-rolled specimens, their  $T_r$  monotonously decreases to 505 K as  $\epsilon$  increases up to 89%. At higher  $\epsilon$ , it remains unchanged rather than increases. Figure 3(d) shows the released energy per unit mass of amorphous phase during structural relaxation,  $E_r$ , as a function of  $\epsilon$ . Considering that the crystalline phases, have precipitated in the amorphous matrix as  $\epsilon > 87\%$  for the RT-rolled specimens and they do not contain the so-called free volume, the crystallized volume fraction was excluded in calculating the  $E_r$  of these specimens. In this case, the  $E_r$  shown in Fig. 3(d) approximately equals the structural relaxation energy per unit mass of specimen divided by the volume fraction of the residual amorphous phase. The volume fraction crystallized,  $x(\epsilon)$ , for the RT-rolled specimen can be estimated by

$$x(\epsilon) = (\Delta H_1 - \Delta H_1(\epsilon)) / (\Delta H_1 + \Delta H_2), \quad (1)$$

where  $\Delta H_1$  and  $\Delta H_2$  are the enthalpies of the first and second exothermic events for the as-cast specimen, respectively, and  $\Delta H_1(\epsilon)$  is the enthalpy of the first exothermic event for the RT-rolled specimen with the thickness reduction  $\epsilon$ . It is indicated that  $E_r$  monotonously increases from 8.5 J/g to 21 J/g in the RT-rolled specimens as  $\epsilon$  changes from 0 to 87%, and then slightly decreases. For the CT-rolled specimens, the increase of  $E_r$  terminates at  $\epsilon = 89\%$ , and then  $E_r$  remains at 29 J/g as  $\epsilon$  further increases.

The shift of  $T_r$  to a lower temperature induced by rolling deformation is consistent with the increase in  $E_r$ . They both indicate the fact that the rolled specimen is in a more disordered high-energy state and possesses a larger driving force for structural relaxation. The lower  $T_r$  and higher  $E_r$  for the CT-rolled specimen, compared with the RT-rolled specimen with the same  $\epsilon$ , demonstrates that the free-volume content and free energy in the CT-rolled specimen are higher than those in the RT-rolled specimen. It is well known that the generation rate of free volume induced by stresses is proportional to the strain rate at high stresses or to the product of stress and strain rate at low stresses.<sup>15</sup> The structural rearrangement, required by the annihilation of free volume, consists of a series of diffusive jumps, and thus the annihilation of free volume is temperature dependent and the rate decreases rapidly with decreasing the temperature.<sup>9</sup>

In the initial stage of deformation, the generation rate is higher than the annihilation rate and the free-volume content increases with the strain, and the net increase rate of free volume at CT-rolling is higher than that at RT-rolling owing to the lower annihilation rate of free volume, which leads to more free volume stored in the CT-rolled specimens compared with the RT-rolled specimen with the same  $\epsilon$ . As the deformation proceeds, the increase in free-volume content puts the amorphous atoms to a higher-energy state, which in turn accelerates the annihilation of free volume, and the net increase rate of free volume will be decreased. An equilibrium is eventually established between generation and annihilation, and the saturation in free-volume content is reached.

We should pay special attention to the variation of free-volume content at high  $\epsilon$ . In our former work, it has been revealed that mechanically driven phase separation will oc-

cur if the  $\epsilon$  in the CT rolling of  $\text{Cu}_{60}\text{Zr}_{20}\text{Ti}_{20}$  BMG exceeds 89%.<sup>12</sup> Our present work indicates that the free-volume content in the CT-rolled specimen reaches saturation just above this deformation degree. Therefore, the occurrence of phase separation can be regarded as a mark at which the increase in free-volume content is terminated, and since then the excess energy provided by rolling deformation is dissipated by phase separation. If crystallization rather than phase separation occurs, just as in the severe plastic deformation of  $\text{Cu}_{60}\text{Zr}_{20}\text{Ti}_{20}$  BMG at RT, the free-volume content not only stops increasing, but also begins to decrease. This is due to the creation of the crystal/amorphous boundaries, where the free volume is apt to annihilate. As the crystalline phases increase in amount, the boundary area per unit volume of specimen rises. As a result, the annihilation rate of free volume increases. So far, it is clear that the increase of free-volume content with the deformation proceeding can be terminated at the occurrence of phase separation or crystallization. Whether such two phenomena are inevitable when the free-volume content reaches saturation in the compressive deformation at temperatures far below the glass transition temperature is unknown, and further investigation is needed.

In summary, the free-volume content in  $\text{Cu}_{60}\text{Zr}_{20}\text{Ti}_{20}$  BMG increases as the rolling deformation proceeds. Due to the depressed annihilation rate of free volume by lowering temperature, the CT-rolled specimen has a higher free-volume content compared with the RT-rolled specimen if the deformation degree is the same. The free-volume content in the CT-rolled specimen is saturated at the occurrence of phase separation, but that in the RT-rolled specimen begins to decrease at the occurrence of crystallization. It is suggested that the crystal/amorphous boundaries can improve the annihilation of free volume and, as a result, the free-volume content decreases as crystallization develops in the deformed specimens.

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