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Effect of cold rolling on glass transition of $Zr_{55}Al_{10}Ni_5Cu_{30}$ bulk metallic glass

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Abstract: $Zr_{55}Al_{10}Ni_5Cu_{30}$ bulk metallic glass was prepared through water-cooled copper mold suction casting, and was rolled up to 95% in thickness reduction. The structures and thermal stabilities of the as-cast and as-rolled specimens were examined by X-ray diffractometer and differential scanning calorimeter. As the thickness reduction increases, the crystallization onset temperature, peak temperature and the apparent activation energy of crystallization almost keep constant, while the glass transition temperature decreases from 681 to 671 K and the apparent activation energy of glass transition increases from (404±26) to (471±29) kJ/mol. The glass transition process is markedly affected by the rolling induced changes of microstructure and structural relaxation.
Key words: bulk metallic glass; cold rolling; glass transition

1 Introduction

In many theoretical approaches, when a liquid is supercooled to a critical temperature where entropies of the liquid and the crystalline solid are identical, a phase transition will take place from the supercooled liquid to a glassy phase if crystallization is suppressed, namely a glass transition[1]. In terms of the free volume model, glass transition is regarded as a kinetic phenomenon depending on competition between the creation and annihilation of the free volume in glasses[2]. Glass transition, one of the important aspects to be considered in applications of amorphous alloys, is affected not only by composition[3−4], mixture enthalpy[5], heat treatment[6−9], and heating rate[10−12], but also by mechanical treatments. An instance is the $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ bulk metallic glass(BMG). Its glass transition temperature T_g slightly increases by 5.6 K/GPa under hydrostatic pressure[13], but drastically decreases by 0.08 K/MPa induced by shear stress during the compression[14]. These phenomena were attributed to the different activation volume of relaxation. As both experiments were performed near T_g, it is difficult to eliminate the effect of phase transformation. In addition, when some BMGs were rolled in the supercooled liquid region[15−16] or at room temperature[17], T_g kept constant or shifted to lower temperature with the thickness reduction increasing, although nanocrystals were observed in all the specimens after deformation. So, the relation between deformation and glass transition is still a matter of debate up to now.

$Zr_{55}Al_{10}Ni_5Cu_{30}$ BMG possesses good stability in structure. Our previous investigation showed that no phase transformations such as crystallization and phase separation occur while it was rolled at the strain rate of 3.0×10^{-1} s^{-1} up to a deformation degree of 95%[18]. Therefore, in order to eliminate the effect of phase transformation on the results, $Zr_{55}Al_{10}Ni_5Cu_{30}$ BMG is chosen to investigate the effect of cold rolling on glass transition.

2 Experimental

The master alloy ingot of $Zr_{55}Al_{10}Ni_5Cu_{30}$ (molar fraction, %) was prepared by arc melting a mixture of pure Zr(99.9%), Al(99.99%), Ni(99.98%) and Cu(99.98%) in a water-cooled copper crucible in a Ti-gettered argon atmosphere. The alloy ingot was remelted several times to ensure compositional homogeneity.

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Samples were produced by suction casting in a water-cooled copper mold, and had a plate-like shape with a cross-section of 1 mm×10 mm and a length of 60 mm. The plates were cut into several segments of 1 mm× 3 mm×10 mm for rolling. The rolling apparatus consists of two rollers of 100 mm in diameter. Covered by two steel plates of 1 mm in original thickness, the specimen was repeatedly rolled in one direction until the desired deformation was obtained. The degree of deformation was denoted by the reduction in thickness, $\varepsilon=(h_0-h)/h_0$, where h_0 and h represent the specimen thicknesses before and after rolling, respectively. Many small deformation passes were used with a progressively narrowing gap between the two rollers. The decrease of the gap during deformation was carefully controlled so that the strain rate was about 3.0×10^{-1} s^{-1}.

The structural natures of the as-cast and as-rolled specimens were examined using a Thermo ARL X-ray diffractometer(XRD) with Cu K_α radiation. The thermal analyses were performed using a Perkin-Elmer Pyris Diamond differential scanning calorimeter(DSC) in a heating rate range from 10 to 80 K/min under a flow of high-purity Ar atmosphere.

3 Results and discussion

Fig.1 shows the continuous DSC traces of the as-cast $Zr_{55}Al_{10}Ni_5Cu_{30}$ specimens and those rolled up to different strains at a heating rate of 20 K/min. Each DSC trace exhibits the endothermic characteristic of glass transition followed by a supercooled liquid region and an exothermic reaction due to crystallization at higher temperature. The values of parameters, such as the glass transition temperature T_g, crystallization onset temperature T_x, crystallization peak temperature T_p and supercooled liquid region ΔT_x, are listed in Table 1. The T_g, T_x, T_p and ΔT_x for the as-cast specimen are 681, 764, 767.5 and 83 K, respectively. After cold rolling, T_g obviously decreases, while T_x and T_p remain almost unchanged.

Fig.2 displays the XRD patterns of the as-cast specimen and that rolled up to ε=95%. Typical peaks of amorphous phase are observed; meanwhile, no clear difference can be identified between the two specimens.

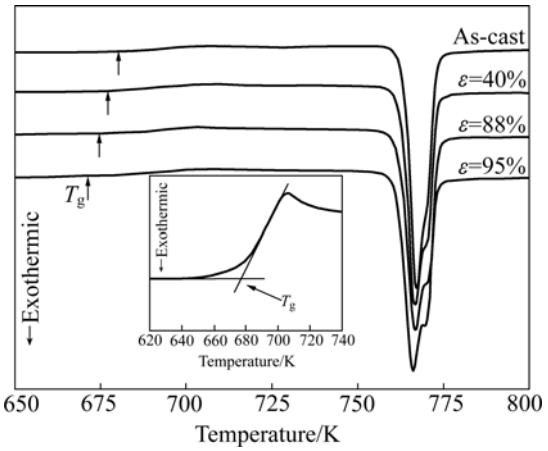

Fig.1 DSC curves of as-cast $Zr_{55}Al_{10}Ni_5Cu_{30}$ specimens and those rolled up to different strains at heating rate of 20 K/min (Inset is definition of glass transition temperature)

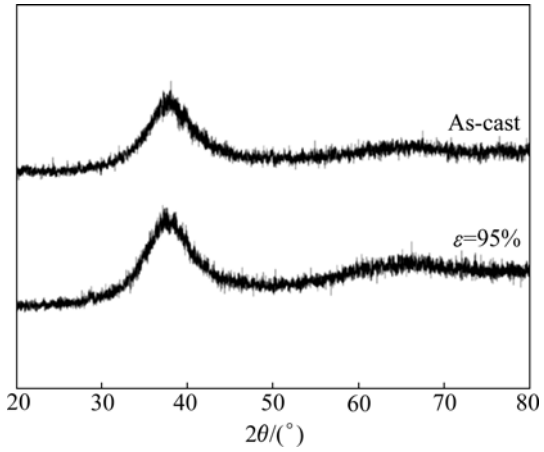

Fig.2 XRD patterns of as-cast $Zr_{55}Al_{10}Ni_5Cu_{30}$ specimen and that rolled up to ε=95%

The HRTEM observations also confirm that the two specimens are completely amorphous (the result is not shown here).

Fig.3 shows the continuous DSC curves of the as-cast $Zr_{55}Al_{10}Ni_5Cu_{30}$ BMG at a heating rate of 10, 20, 40 and 80 K/min, respectively. T_g, T_x and T_p increase with increasing the heating rate. Similar trends exist on the DSC curves of the specimen rolled up to ε=95%. The apparent activation energy E_i for a reaction can be

Table 1 Thermodynamic and kinetic parameters of as-cast $Zr_{55}Al_{10}Ni_5Cu_{30}$ specimens and those rolled up to different strains (T_g, T_x, T_g^p and T_p are measured at heating rate of 20 K/min)

Sample	T_g/K	T_g^p/K	T_x/K	T_p/K	ΔT_x/K	E_g/(kJ·mol^{-1})	E_p/(kJ·mol^{-1})
As-cast	681	705	764	767.5	83	404±26	334±11
ε=40%	678	705	764	766.7	86	−	−
ε=88%	675	705	762	766.2	87	−	−
ε=95%	671	704	761	766.1	90	471±29	344±8

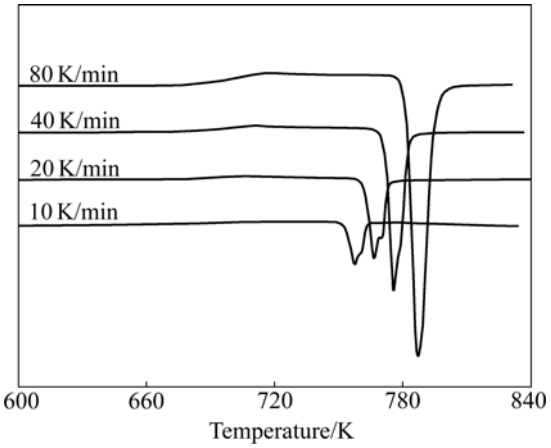

Fig.3 DSC traces for as-cast $Zr_{55}Al_{10}Ni_5Cu_{30}$ specimen at different heating rates

calculated by Kissinger's equation[19]:

$$\ln\frac{T_i^2}{\beta}=\frac{E_i}{RT_i}+C_i \quad (1)$$

where β is the heating rate; T_i is the characteristic temperature of the reaction; R is the gas constant; and C_i is a constant for the reaction. The Kissinger plots of the glass transition and crystallization for the as-cast specimen and the rolled specimen with ε=95% are shown in Fig.4. The apparent activation energies of the glass transition E_g and the crystallization E_p derived from the slope of the Kissinger plots are listed in Table 1. E_g and E_p of the as-cast BMG are (404±26) and (334±11) kJ/mol, respectively. After the specimen is rolled up to 95%, E_p remains almost unchanged considering the experimental error, while E_g increases to (471±29) kJ/mol.

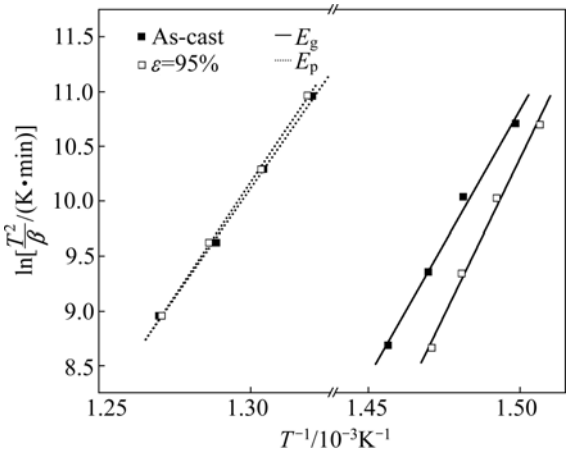

Fig.4 Kissinger plots of glass transition and crystallization for as-cast $Zr_{55}Al_{10}Ni_5Cu_{30}$ specimen and that rolled up to ε=95%

From Table 1, it is known that T_x, T_p and E_p are almost invariable even when the thickness reduction is up to 95%, indicating that cold rolling has a little effect on the crystallization of the BMG. However, cold rolling has a considerable influence on the glass transition.

According to the model proposed by COHEN and GREST[20] and WANG et al[21], a metallic glass is heterogeneous in structure, consisting of liquid-like regions with large free volume or high local free energy, and solid-like regions with small free volume or low free energy. In contrast to solid-like regions, the transition from liquid-like regions to supercooled liquid state would occur earlier, and needs less energy. That is to say, the glass transition of liquid-like regions can take place at lower temperature than solid-like regions. The deformation mode of metallic glasses comprises homogeneous deformation that occurs at low strain rate and high temperature, and inhomogeneous deformation that occurs at high strain rate and low temperature. During inhomogeneous deformation, the strain is highly localized in narrow deformation regions, i.e. shear bands [22]. These bands contain more free volume than the matrix[23], which means that shear bands contain more liquid-like region than matrix. The deformed metallic glass, without phase transition, can be treated as a composite of hard undeformed amorphous grains surrounded by soft shear band boundaries. The increase of shear-band density would improve the liquid-like region content of the "composite". There is a linear relation between the shear-band density and the plastic strain[23], i.e., the shear-band density increases with the increasing thickness reduction during the cold rolling process, which means that the fraction of liquid-like region increases in the BMG. As a result, T_g shifts to a lower temperature for the as-rolled specimens.

Metallic glasses undergo phase separation, structural relaxation, glass transition, nucleation and growth of nuclei during a continuous heating process. As done in other work[11], T_g, in the present paper, is defined on the DSC curves as the point of intersection between the linearly extrapolation curve below the glass transition and the steepest tangent of the rise in the heat flow signal (see inset in Fig.1). Thus, the apparent glass transition activation energy, E_g, should include the activation energies of phase separation, structural relaxation and "real" glass transition. In the isothermal annealing of the $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG in the glass transition region, phase separation and structural relaxation occur prior to glass transition, so E_g decreases[8]. In contrary to the isothermal annealing, the cold rolling is helpful to enhancing the structural relaxation enthalpy, as found in the rolled $Cu_{60}Zr_{20}Ti_{20}$ BMG[24]. In the present work, no phase transformation is detected in the rolled $Zr_{55}Al_{10}Ni_5Cu_{30}$ BMG, but the structural relaxation enthalpy becomes more obvious (Fig.5). From the enthalpy recovery method(ERM)[14], the structural relaxation enthalpy is strongly dependent

on the initial state of the glassy sample before the DSC measurement, while the "real" glass transition is not sensitive to the initial glassy state. Table 1 shows that the overshoot peak temperature, T_g^p, during glass transition, which could be used to characterize approximately the "real" glass transition process, keeps almost invariable with increasing the thickness reduction. So, it is speculated that the cold rolling has no effect on the "real" glass transition. The rolling induced increase of E_g might come from the enlarged structural relaxation enthalpy.

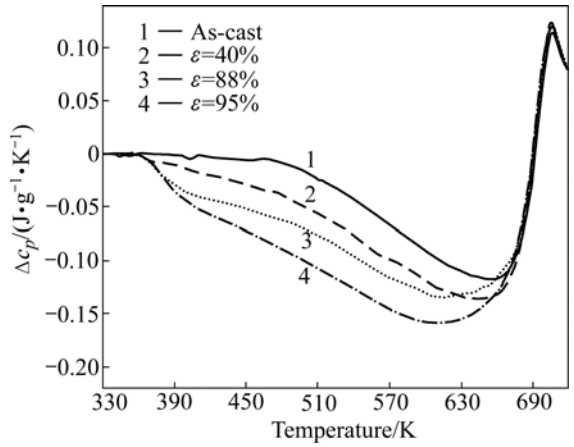

Fig.5 Specific heat capacity of as-cast $Zr_{55}Al_{10}Ni_5Cu_{30}$ specimens and those rolled up to different strains at heating rate of 20 K/min

4 Conclusions

1) $Zr_{55}Al_{10}Ni_5Cu_{30}$ BMG was rolled at a strain rate of 3.0×10^{-1} s^{-1} up to a deformation degree of 95% at room temperature. With increasing the thickness reduction, T_g decreases from 681 to 671 K, and E_g increases from (404±26) to (471±29) kJ/mol.

2) The decrease of T_g is due to the presence of many shear bands. The rise of E_g can be ascribed to the enlarged structural relaxation enthalpy.

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