Deformation behavior of $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ glassy alloy with wide supercooled liquid region

Yoshihito Kawamura,[a] Tsutomu Shibata, Akihisa Inoue, and Tsuyoshi Masumoto
Institute for Materials Research, Tohoku University, Sendai 980-77, Japan

(Received 8 April 1996; accepted for publication 13 June 1996)

We report the stress-strain behavior for a $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ (at.%) glassy alloy with a significant supercooled liquid region of 105 K. The transition temperature from inhomogeneous deformation to a homogeneous one increases with increasing strain rate. The alloy in the supercooled liquid state, however, exhibited the homogeneous deformation even at higher strain rates above 0.5 s^{-1}. The strength was also dependent on the strain rate and independent of temperature in the inhomogeneous deformation region, and was sensitive to both strain rate and temperature in the homogeneous region. The stress-strain curves in the homogeneous deformation mode were accompanied by a stress overshoot and its height increases with increasing temperature and strain rate. © *1996 American Institute of Physics.* [S0003-6951(96)00835-2]

Engineering application fields of amorphous alloys have been limited because of the limitation of alloy size and the lack of workability and machinability. Recently, a number of glassy alloys with a wide supercooled liquid region above 60 K and high glass-forming ability have been discovered in Zr-based alloys.[1–3] These glassy alloys promise to allow the production of large-scale bulk glassy materials by consolidation of glassy powders[4–8] and casting at low cooling rates.[1–3] Availability of the bulk glassy alloys with a wide supercooled liquid region enables unique approaches for shaping and forming into complex-shaped components through significant viscous flow inherent to the supercooled liquid. The deformation of the glassy alloys is divided into two modes, namely, homogeneous mode and inhomogeneous mode.[9–14] Deformation behavior such as the temperature and strain-rate dependence of the deformation mode and flow stress is essential to the performance of the forming and shaping of the bulk glassy alloys. In this letter, we report the deformation behavior of a $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ (at.%) glassy alloy with a significant supercooled liquid region of 105 K.

A $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ glassy alloy ribbon with a cross section of about 1.0×0.02 mm^2 was produced by a single-roller melt-spinning method. The formation of a single amorphous phase was confirmed by x-ray diffractometry and transmission electron microscopy (TEM). The thermal properties of the glassy alloy were measured by a differential scanning calorimetry (DSC). The glass transition temperature (T_g), crystallization temperature (T_x), and supercooled liquid region ($\Delta T_x = T_x - T_g$) of the $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ glassy alloy are 652, 757, and 105 K, respectively, at a continuous heating rate of 0.67 K/s. The time-temperature-transformation (T-T-T) curve revealing the onset of crystallization for the $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ glassy alloy has been previously reported.[8] The duration of retaining the amorphous phase without decomposition is 15 000 s at 673 K, 2000 s at 693 K, and 320 s at 713 K. These provide the time window for the working of this alloy at the supercooled liquid state. The tensile tests were conducted using an Instron-type tensile test apparatus. The gauge length was 10 mm.

Figure 1(a) shows the temperature dependence of the stress-strain curve at a strain rate of 5.0×10^{-4} s^{-1} for the $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ glassy ribbon. The deformation mode changes from inhomogeneous type to homogeneous one at around 533 K. In the homogeneous deformation regime, the strength decreases and the elongation increases with increasing temperature. Figure 1(b) shows the strain-rate dependence of the stress-strain curve at a temperature of 653 K which is close to T_g (652 K). The strength increases and the elongation decreases with strain rate. The homogeneous mode of deformation, moreover, changes to inhomogeneous type at a higher strain rate (5.0×10^{-1} s^{-1}).

Figure 2(a) shows the temperature and strain rate depen-

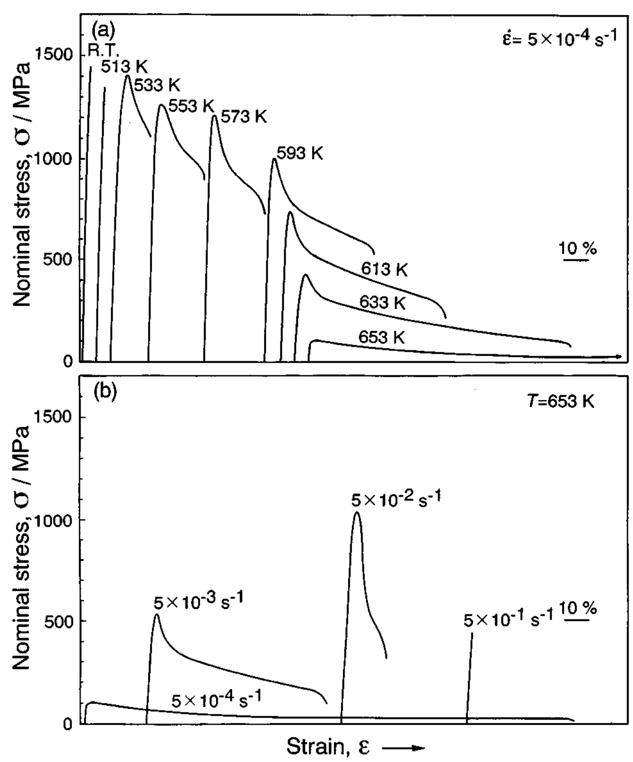

FIG. 1. Changes in the stress-strain curves as a function of testing temperature at $5.0\times 10^{-4} s^{-1}$ (a) and as a function of strain rate at 653 K (b) for $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ glassy alloy.

[a]Electronic mail: rivervil@imr.tohoku.ac.jp

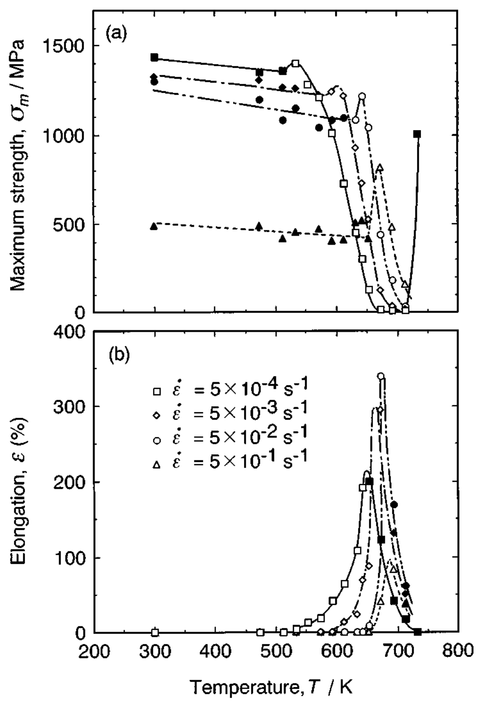

FIG. 2. Testing temperature and strain rate dependence of the maximum tensile strength (a) and the elongation (b) for $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ glassy alloy. The open and solid symbols in (a) represent the alloys to be deformed homogeneously and inhomogeneously, respectively. The alloys indicated with the open and solid symbols in (b) have good ductility and brittle nature, respectively, at room temperature after testing.

dence of the tensile strength for the $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ glassy ribbon. With increasing temperature, the deformation mode changes from the inhomogeneous type to a homogeneous one at a certain temperature. This critical temperature depends upon the strain rate. In the inhomogeneous regime, the strength has very weak temperature dependence and strong strain rate sensitivity. On the other hand, the strength in the homogeneous region depends on both the temperature and strain rate. The strength reveals a peak at first stage when the deformation mode changes to homogeneous type, and then decreases suddenly with increasing temperature. At higher strain rates, this tendency is shifted towards higher temperatures and the peak in strength becomes higher. Figure 2(b) shows the temperature and strain rate dependence of the elongation. The samples with good ductility show bending through 180° without fracture. The brittle nature in some of the samples are due to crystallization or structural relaxation during tensile test. The glassy alloy is significantly elongated in the homogeneous deformation mode in which the elongation is dependent on both the temperature and strain rate. As the temperature increases, the elongation increases, reaches a peak, and then decreases. This decrease in the elongation at higher temperatures is due to the crystallization or structural relaxation during tensile test. The peak in the elongation is shifted towards higher temperatures with increasing strain rate.

One should not overlook that the deformation in the homogeneous region begins to yield with a maxima, namely, a stress overshoot, and then transfers to stable flow as shown in the stress-strain curves (Fig. 1). The height of the stress

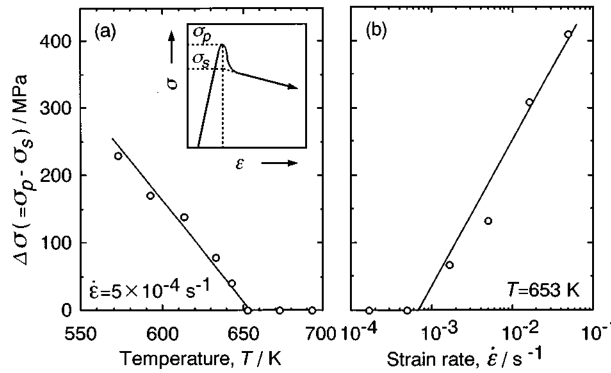

FIG. 3. Changes in the stress over shoot $\Delta\sigma$, which is the difference between the peak stress σ_p and the stable stress σ_s as shown in the inset, as a function of testing temperature at a strain rate of 5×10^{-4} s^{-1} (a), and as a function of strain rate at 653 K (b) for $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ glassy alloy.

overshoot $\Delta\sigma$, which is the difference between the peak stress σ_p and the stable flow stress σ_s, decreases with increasing temperature and decreasing strain rate as shown in Fig. 3. This phenomenon is closely related to the discontinuous changes in the temperature dependence of the maximum strength at the transition temperature of homogeneous deformation as shown in Fig. 2(a). Little attention has been given to the stress overshoot, although such stress-strain curves were observed in some metallic glasses such as Pd-, Mg-, and La-based alloys.[7,15,16] The stress overshoot seems to be unexplainable by a change in sample shape such as necking because the phenomenon is also observed under compressive loading.[7] The dislocation theory applied to crystalline materials is, moreover, inapplicable to the glassy alloys. The stress overshoot can, however, be explained by viscoelastic properties including relaxation.[17]

Figure 4 shows the temperature and strain-rate dependence of the maximum strength and deformation mode for the $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ glassy alloy. As the strain rate increases, the maximum strength increases in the homogeneous mode and then the deformation mode changes to in-

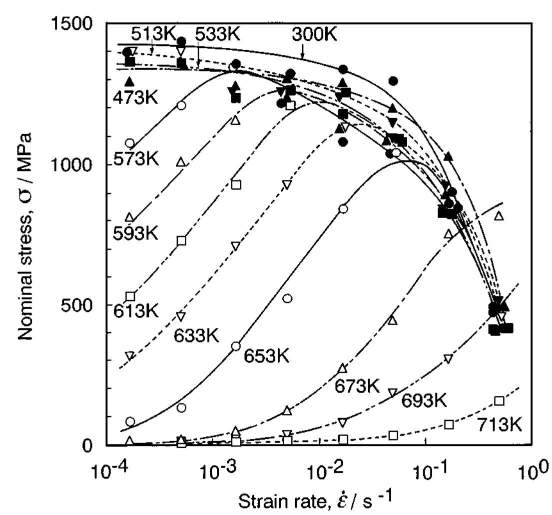

FIG. 4. Testing temperature and strain rate dependence of the maximum tensile strength and deformation mode for $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ glassy alloy. The open and solid symbols represent the alloys to be deformed homogeneously and inhomogeneously, respectively.

homogeneous type, and the maximum strength decreases in the inhomogeneous mode. The critical temperature, where the deformation mode changes from the homogeneous type to the inhomogeneous one, is shifted towards higher strain rates with increasing temperature. The homogeneous deformation mode in the stable supercooled liquid region above 673 K, however, remains unchanged as is seen even at a higher strain rate of 0.5 s^{-1}. The present results suggest that the deformation mechanism changes at T_g. In the two deformation modes there are distinct differences in the strain rate and temperature dependence of the maximum strength. In the inhomogeneous region, the strength has very weak temperature dependence and strong strain rate sensitivity, resulting in an identical strength within the accuracy of 20% at each strain rate. The strain rate dependence of the strength is slight at the strain rates up to 5.0×10^{-2} s^{-1} and significant in the higher strain rate range. On the other hand, in the homogeneous region the strength is very sensitive to both the temperature and strain rate. The strength decreases with increasing temperature and decreasing strain rate.

The macroscopic deformation of amorphous alloys depends on the viscoelastic behavior where the role of viscosity becomes predominant at high temperature, low strain rate, and low stress as compared with that of elasticity. The deformation mechanisms of amorphous alloys have been described with free volume model, dislocation model and atomic-level stresses.[18] These models do not clearly describe the macroscopic stress-strain behavior in wide ranges of strain rate, stress, and temperature (below, through, and above T_g). We need further investigation of macroscopic stress-strain and viscoelasticity, and atomic-level deformation mechanisms by both experiments and computer simulations. The $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ glassy alloy seems to be a suitable material for the investigation because the alloy has a stable supercooled liquid state. We are carrying out additional studies of the macroscopic deformation by investigations of stress-strain behavior, static and dynamic viscoelastic behavior, structural relaxation, and diffusivity.

To summarize, we have revealed the deformation behavior of the $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ glassy alloy with a wide supercooled liquid region. The deformation mode depended on both strain rate and temperature in the temperature range below T_g. The higher temperature and lower strain rate revealed homogeneous deformation. The alloy in the supercooled liquid state was moreover, deformed homogeneously even at high strain rates above 0.5 s^{-1}. The strength is dependent on strain rate and independent of temperature in the inhomogeneous deformation mode, and is very sensitive to both strain rate and temperature in the homogeneous deformation mode. In the homogeneous deformation region, the strength becomes lower at higher temperature and lower strain rate. The stress-strain curves in the homogeneous deformation were also accompanied by a stress overshoot whose height increases with decreasing temperature and increasing strain rate. The utilization of the supercooled liquid enables the working and forming at high strain rates under low pressures. The present results seem to promise further development of the glassy alloy with a wide supercooled liquid region as a new material with high strength and good workability.

[1] T. Masumoto, Mater. Sci. Eng. A **A181/A182**, 8 (1994).
[2] A. Inoue, T. Zhang, and T. Masumoto, Mater. Trans. JIM **36**, 391 (1995).
[3] A. Peker and W. L. Johnson, Appl. Phys. Lett. **63**, 2342 (1993).
[4] D. G. Morris, Mater. Sci. **14**, 215 (1980).
[5] Y. Kawamura, M. Takagi, M. Akai, and T. Imura, Mater. Sci. Eng. **98**, 449 (1988).
[6] Y. Kawamura, M. Takagi, M. Senoo, and T. Imura, Mater. Sci. Eng. **98**, 415 (1988).
[7] Y. Kawamura, A. Inoue, and T. Masumoto, J. Jpn. Soc. Powder Powder Metall. **38**, 110 (1991).
[8] Y. Kawamura, H. Kato, A. Inoue, and T. Masumoto, Appl. Phys. Lett. **67**, 2008 (1995).
[9] T. Masumoto and R. Maddin, Acta Metall. **19**, 725 (1971).
[10] R. Maddin and T. Masumoto, Mater. Sci. Eng. **9**, 1534 (1972).
[11] F. Spaepen, Acta Metall. **25**, 467 (1977).
[12] H. S. Chen, J. Non-Cryst. Solids **27**, 257 (1979).
[13] A. S. Argon, Acta Metall. **27**, 47 (1979).
[14] A. I. Taub, Acta Metall. **28**, 663 (1980).
[15] A. Inoue. T. Nakamura, N. Nishiyama, and T. Masumoto, Mater. Trans. JIM **33**, 937 (1992).
[16] A. Inoue. T. Zhang, and T. Masumoto, Mater. Trans. JIM **31**, 425 (1990).
[17] B. Maxwell and M. Nguyen, Polym. Eng. Sci. **19**, 1140 (1979).
[18] J. C. M. Li, in *Rapidly Solidified Alloys,* edited by H. H. Liebermann (Marcel Dekker, New York, 1993), p. 379.