SUPERPLASTIC DEFORMATION AND VISCOUS FLOW IN AN Zr-BASED METALLIC GLASS AT 410°C

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ABSTRACT

The thermal properties of an amorphous alloy (composition in at.%: Zr–10Al–5Ti–17.9Cu–14.6Ni), and particularly the glass transition and crystallization temperature as a function of heating rate, were characterized using Differential Scanning Calorimetry (DSC). X-ray diffraction analyses and Transmission Electron Microscopy were also conducted on samples heat-treated at different temperatures for comparison with the DSC results. Superplasticity in the alloy was studied at 410°C, a temperature within the supercooled liquid region. Both single strain rate and strain rate cycling tests in tension were carried out to investigate the deformation behavior of the alloy in the supercooled liquid region. The experimental results indicated that the alloy did not behave like a Newtonian fluid.

INTRODUCTION

Metallic glasses fabricated by rapid quenching from the melt were first discovered in 1960 [1]. Because of the high quench rate requirements (10^4 – 10^6 K/s), only thin ribbons and sheets with a thickness less than 0.1 mm could be fabricated. One of the most important recent developments in the synthesis of amorphous materials is the discovery that certain metallic glasses can be fabricated from the liquid state at cooling rates of the order of 10 K/s. This enables the production of bulk amorphous alloys with a thickness of ~10 mm. While advances in amorphous metallic alloy development have been impressive, they have been made largely through empirical approaches. Amorphous alloys in bulk form can be characterized, in fact, by some empirical rules [2]: (a) multi-components (at least three, and very often five components), (b) a large difference in atomic size, (c) "deep" eutectics in phase diagrams of the alloys, and (d) a large value of $\Delta T = T_x - T_g$ (T_x and T_g are the crystallization and glass transition temperatures, respectively).

Bulk amorphous alloys have many potential applications resulting from their unique properties. Among those worth mentioning are: superior strength and hardness, excellent corrosion resistance [3], shaping and forming in a viscous state [4], reduced sliding friction and improved wear resistance [5], and extremely low magnetic energy loss. These properties should lead to applications in the fields of near-shape fabrication by injection molding and die casting, coatings, joining and bonding, biomedical implants, and synthesis of nanocrystalline and composite materials [2]. Also, the development of bulk amorphous alloys with soft magnetic properties would be extremely beneficial for energy conservation.

The mechanical behavior of metallic glasses is characterized by either inhomogeneous or homogeneous deformation. Homogeneous deformation usually takes place at high temperatures ($>0.70T_g$) [6], and the material can often exhibit significant plasticity. The transition temperature T_{tr} from inhomogeneous to homogeneous deformation (or brittle-to-ductile transition) is strongly dependent upon strain rate. For example, T_{tr} for a $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ alloy is about 533K (corresponding to $0.82T_g$) at 5×10^{-4} s^{-1}, but is 652K (corresponding to $1.0T_g$) at 5×10^{-2} s^{-1} [4]. The strain rate dependence of T_{tr} (480–525K; 0.61–$0.75T_g$) has also been demonstrated in $Fe_{40}Ni_{40}B_{20}$ [7]. These results suggest that homogeneous deformation is associated with certain diffusional relaxation processes.

As early as 1980, Homer and Eberhardt [8] reported the observation of superplasticity in amorphous $Pd_{78.1}Fe_{5.1}Si_{16.8}$, in ribbon form, ($T_g$=395°C, T_x=410°C) during non-isothermal creep experiments. In their experiments, test samples were rapidly heated to the maximum temperature of 425°C under a constant load (stress range: 25–150 MPa). The resulting creep rate was rather high; for example, an applied stress of 150 MPa produced a creep rate of 0.5 s^{-1}. The strain rate sensitivity value was estimated to be about one, suggesting possible Newtonian flow. Since the test temperature of 425°C was higher than T_x, a dispersion of 0.4 μm crystalline grains in

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an amorphous matrix was observed in the alloy after superplastic deformation. It is of particularly importance to note that slow heating during creep testing resulted in the disappearance of superplasticity. This was apparently caused by the structural instability of this alloy, as indicated by a narrow ΔT (=15°C), and correspondingly fast crystallization kinetics.

Zelenskiy *et al.* [9] studied the formability of amorphous $Co_{68}Fe_7Ni_{13}Si_7B_5$ (T_g=563°C, T_x=583°C) at temperatures between 500 and 640°C. They observed large tensile ductility at a relatively fast strain rate of 10^{-2} s^{-1} in the 550–580°C temperature range (i.e. within the supercooled liquid region). Specifically, the maximum elongation of 180% was recorded at a corresponding minimum stress of about 150 MPa. However, the strain rate sensitivity was not measured. TEM microstructural examination indicated that annealing at 580°C resulted in the precipitation of nanometer grains (~50–70 nm) in the alloy. From these results, the authors argued that the presence of a large grain/amorphous matrix interfacial area was necessary for superplasticity. However, we want to point out that this may not be the case. In fact, several pieces of experimental evidence have indicated a reduced ductility in the presence of nanograins [4, 8]. A recent study of Busch et al [10] also showed that the viscosity of a metallic glass increases sharply once it is heated over the crystallization temperature. As expected, this increase in

observations. First, superplasticity occurs in alloys with a large ΔT; typically, about several tens of degrees. The larger the ΔT ($=T_x-T_g$), the larger the tensile elongation, provided tests were conducted in the supercooled liquid region. This indicates the importance of thermal stability of a metallic glass during superplastic deformation. They also noticed that an increased heating rate usually produced an increased elongation. Apparently, this is associated with structural stability since slow heating rates result in an earlier onset of crystallization.

In studying the formability of a $La_{55}Al_{25}Ni_{20}$ alloy, Inoue *et al* [12, 13] reported that the alloy in the supercooled liquid range (480-520K) behaved like a Newtonian fluid, i.e., m=1. A tensile elongation of over 15,000% was recorded at 500K at a strain rate of 10^{-1} s^{-1}. However, a careful examination of their stress-strain rate data indicated that the strain rate sensitivity tends to decrease to less than one when the testing temperature (e.g. 510, 520K) approaches T_x. Again, this is due to a partial crystallization in the amorphous structure during testing.

Kawamura *et al* [4] recently studied the high-temperature deformation of a $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ metallic glass with a wide range of ΔT (T_g=652K, T_x=757K). In the supercooled liquid region, they found that plastic flow was strongly dependent on strain rate and the strain rate sensitivity value exceeded 0.8, but was less than unity. The high strain rate sensitivity produced a corresponding high tensile elongation. For example, a tensile elongation of 340% was obtained at a strain rate of 5×10^{-2} s^{-1} and at 673K. However, true Newtonian behavior (m=1) was not observed in the alloy. As discussed before, the structure of a supercooled liquid is thermally unstable. Upon thermal exposure, and particularly under an external applied stress, the amorphous structure tends to crystallize. It is believed that the observation of an m value of less than 1 can be attributed to the fact that the deformation mode of the alloy, to a first-order approximation, is a mixture of Newtonian flow (m=1) and fine-grained superplasticity (m=0.5). Under appropriate testing conditions, both deformation modes are expected to give rise to a large tensile elongation.

To investigate further superplasticity in metallic glass systems, Kawamura *et al* [4] tested a $Pd_{40}Ni_{40}P_{20}$ alloy prepared by rapid solidification. Within the range of 560-620K, the alloy exhibited similar deformation behavior to that of $Zr_{65}Al_{10}Ni_{10}Cu_{15}$; namely, a high-strain-rate-sensitivity value accompanied by extended tensile ductility in the supercooled liquid region (T_g=578-597K, T_x=651K). In contrast to $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ which is non-Newtonian, $Pd_{40}Ni_{40}P_{20}$ can behave like a true Newtonian fluid (i.e. m=1) under appropriate testing conditions. The difference may be associated with the fact that $Pd_{40}Ni_{40}P_{20}$ is more thermally stable than $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ in the supercooled liquid state, as pointed out by Kawamura *et al* [14]. (ΔTs are 72 and 100K for $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ and $Pd_{40}Ni_{40}P_{20}$, respectively.) Therefore, during high-temperature deformation, $Pd_{40}Ni_{40}P_{20}$ can retain its amorphous state, whereas crystallization may already have taken place in $Zr_{65}Al_{10}Ni_{10}Cu_{15}$. This is indirectly indicated by the fact that the viscosity of $Pd_{40}Ni_{40}P_{20}$ is about one order of magnitude lower than that of $Zr_{65}Al_{10}Ni_{10}Cu_{15}$.

Despite the fact that metallic alloys still have a high strain rate sensitivity at a temperature that approaches T_x, the tensile elongation reduces rapidly. This appears to be contrary to the general idea that an ultrafine grain size alloy is expected to give rise to a large elongation, presumably as a result of extensive grain boundary sliding. However, it must be pointed out that in the case of grain boundary sliding, the sliding strain must be properly accommodated either by diffusional flow or by dislocation slip (e.g., climb or glide) across neighboring grains, in order to prevent cavitation and, thus, fracture [15]. Dislocation slip in an ordered, multicomponent intermetallic compound is difficult even at temperatures near T_x (~0.8 T_m, where T_m is the melting point of the alloy). Also, at a relatively high strain rate of ~10^{-2} s^{-1}, diffusional processes are not expected to be sufficiently fast to accommodate sliding strain. This may offer an explanation for a high m value but an associated low tensile elongation in metallic glasses at temperatures in the vicinity of T_x. It is noted that, for the case of pure Newtonian flow, no such accommodation is needed.

In summary, large tensile ductilities can be obtained in the supercooled liquid region from a metallic glass with a large ΔT. The maximum ductility is expected to occur at a temperature near T_x, where the flow stress (or viscosity) is low, and at a high strain rate at which the alloy can retain its amorphous structure during deformation. The purpose of this paper is to investigate the deformation behavior of an amorphous Zr-10Al-5Ti-17.9Cu-14.6Ni alloy in the supercooled liquid region.

EXPERIMENTS

The material used in the present study has a composition of Zr-10Al-5Ti-17.9Cu-14.6Ni and was developed at Caltech [16]. Zone-purified Zr bars (containing 12.3 appm O and 10 appm Hf), together with pure metal elements, were used as charge materials. The alloys were prepared by arc melting in inert gas, followed by drop casting into 7.0-mm-diameter by 7.2cm-long Cu molds at Oak Ridge National Laboratory. The details of fabrication of the alloy have been described previously [16].

Tensile sheet specimens were fabricated from the as-cast material by means of electrical discharge machining. They had a gage length of 4.76 mm, a thickness of 1.27 mm and a width of 1.59 mm, as shown in FIG01. Tensile tests were conducted using an Instron machine equipped with an air furnace. Due to structural instability during testing of samples at high temperatures, the heating rate must be rapid to minimize crystallization. Typically, the heating plus holding time prior to testing was about 25 minutes. For example, for test at 410°C and a constant strain rate of 10^{-2} s^{-1}, the temperature profile was: 305°C (5 min), 371°C (10 min), 397°C (15 min), 407°C (20 min), 410°C (23 min), and 410°C (24 min). Constant strain rate tests were performed with a computer-controlled machine at a strain rate of 10^{-2} s^{-1}. Strain-rate-cycling tests were also performed between 10^{-3} and 10^{-2} s^{-1} to measure strain rate sensitivity exponents.

Differential scanning calorimetry (DSC) was used to characterize the thermodynamic and kinetic properties of the amorphous alloy. Various heating rates of 10, 20, 40, and 80K per minute were used to examine the glass transition and crystallization temperatures as a function of heating rate.

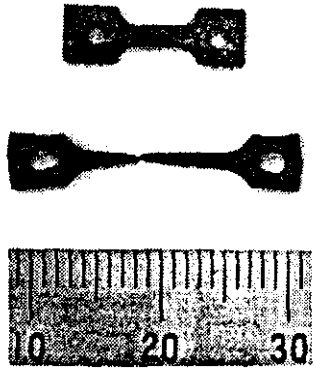

FIG01 Amorphous Zr–10Al–5Ti–17.9Cu–14.6Ni alloy samples fractured in tension in the supercooled liquid region. An untested sample is also shown for comparison.

RESULTS AND DISCUSSION

Differential scanning calorimetry (DSC) curves obtained from the amorphous Zr–10Al–5Ti–17.9Cu–14.6Ni alloy at different heating rates are shown in FIG01. The temperatures for the start (T_g^s) and end (T_g^e) of glass transition, and crystallization (T_x), and supercooled range (ΔT) are listed in Table 1. As expected, these temperatures are all dependent upon the heating rate. In fact, they all increase with an increasing heating rate.

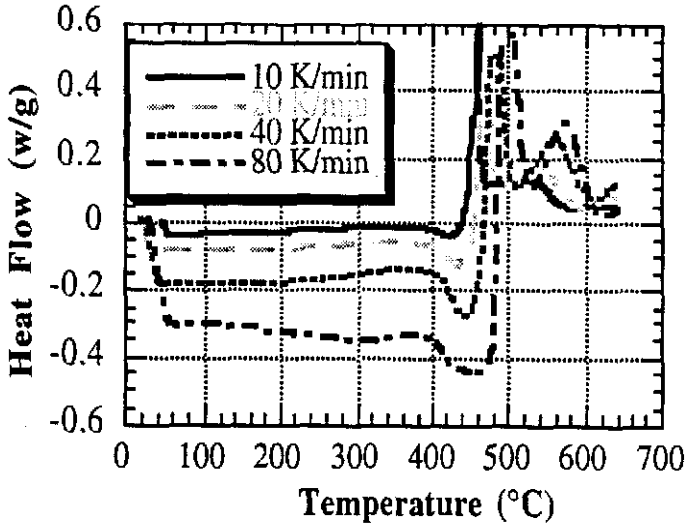

FIG02 DSC curves measured from amorphous Zr–10Al–5Ti–17.9Cu–14.6 Ni alloy at different heating rates.

Table 1 Temperatures for the start (T_g^s) and end (T_g^e) of glass transition, crystallization (T_x), and supercooled range (ΔT) for amorphous Zr–10Al–5Ti–17.9Cu–14.6Ni alloy

Heating rate, (K/min)	T_g^s , K	T_g^e, K	T_x, K	ΔT, K
10	628	696	714	86
20	631	705	729	98
40	637	716	742	105
80	640	728	758	118

The stress-strain curve of the alloy at 410°C and a strain rate of 10^{-2} s^{-1} is shown in Fig. 3. After an initial yield drop, there is an apparent steady-state flow region which is followed by a sharp decrease in flow stress until the final fracture. The initial yield drop usually occurred during condition of high temperature and high strain rate deformation; this behavior has also been observed by Kawamura *et al* [17] who attributed it to a transient phenomenon. The fracture strain is about 1.3 which corresponds to approximately 250% tensile elongation. The fractured sample is noted to exhibit gradual necking, as shown in FIG01, almost necking down to a point. The final decrease in flow stress is, therefore, not a result of softening, but from a reduction in load bearing capacity. The fracture appearance is in contrast to that observed in a $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ metallic glass [4], in which a uniform deformation was observed. This difference may be caused by the fact that the samples used by Kawamura et al were very thin (0.02 mm). As a result, the samples were subject to a plane stress condition. It is of interest to note that the maximum stress is about 700 MPa; this is considerably higher than the flow stresses reported for any existing metal or ceramic exhibiting superplasticity or extended ductility. The flow stress for a superplastic metal or ceramic is typically only about 70 MPa.

To characterize the deformation behavior, a strain-rate-cycling test was carried out to measure the strain rate sensitivity value. The result is shown in FIG04, the values of strain rate sensitivity

m in equation $\sigma = Kr^m$, where r is strain rate, σ is stress, and K is a constant, were measured by strain rate cycling tests between 10^{-2} and 7×10^{-3} s^{-1}. Some observations are readily made. There is no steady state after each strain rate cycle, making it difficult to determine accurately the strain rate sensitivity. This difficulty can probably be attributed to structural instability during testing. It is noted that, despite the fact that 410°C is below the crystallization temperature, an external applied stresses can promote crystallization in amorphous alloys [18]. Thus, it is believed that some nano-scale, crystallized phase evolved during the course of the test. It is known that the presence of nanocrystalline phases can significantly affect the mechanical properties of an metallic glass. For example, Busch *et al* [10] recently showed that the presence of crystalline phases increases the viscosity of a $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ metallic glass. This observation is also consistent with the results of Kim *et al* [19, 20] who reported that the fracture strength of an amorphous $Al_{88}Ni_{10}Y_2$ was doubled if the alloy was crystallized and contained 5-12 nm Al particles. Therefore, in the present strain rate cycle test, a continuous strengthening is proposed to be a result of the continuous precipitation of nanocrystals in the amorphous matrix. In fact, this is also reflected by a slight increase in stress after the initial yield drop (strain >0.4) shown in FIG03.

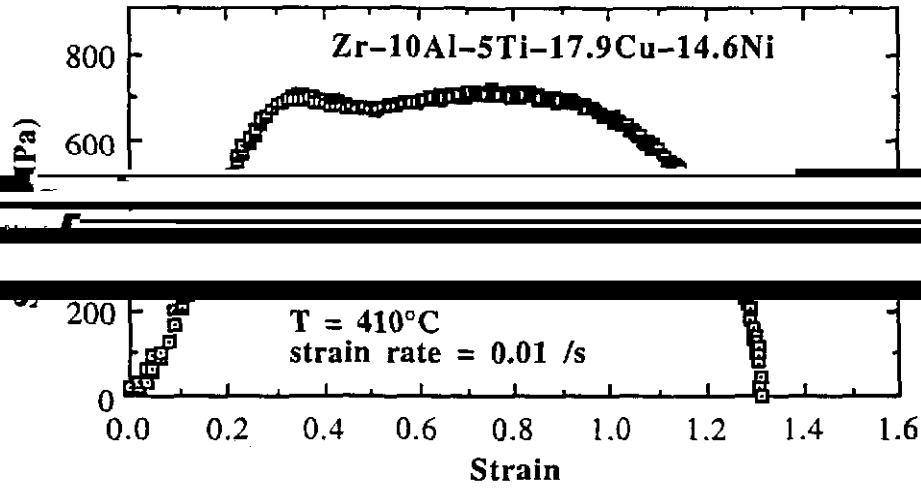

FIG03 Stress-strain curve for amorphous Zr-10Al-5Ti-17.9C

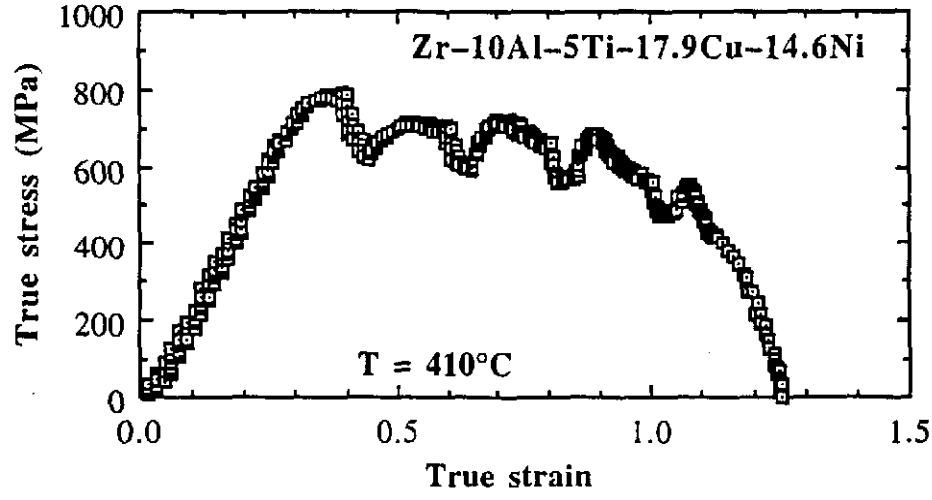

FIG04 Results from a strain-rate-cycling test at 410°C.

It is noted in FIG04 that, after each strain rate decrease, except for the first one, there is no steady-state flow region. The gradual decrease in flow stress after decreasing the strain rate results from sample necking. Data from FIGs03 and 04 indicate that significant sample necking occurs at a strain of approximately 0.7-0.8, as discussed previously. The fracture strain obtained in the strain-rate-cycling test is similar to that in a constant strain rate test.

From the above results, it may be tentatively concluded that the strain-rate-cycling test, which is commonly used for measuring strain rate sensitivity values, and thus inferring deformation mechanism in superplastic polycrystalline alloys, may be an inappropriate method for metallic glasses. This is because the structure of a metallic glass is unstable compared to that of a fine-grained superplastic alloy, especially under stress.

It is worth noting that from FIG04 the average "apparent" strain rate sensitivity for the present alloy is computed to be about 0.5. Although structural instability can contribute to some variations in determining the "true" strain rate sensitivity value, its influence is not expected to be sufficiently great to imply a "true" strain rate sensitivity value of as high as one. In other words, the present alloy does *not* behave like a Newtonian fluid. The non-Newtonian behavior is also reflected by the fracture appearance of tested samples (FIG01). The deformation behavior of an ideal Newtonian fluid is, in principle, uniform and would not be expected to exhibit significant local necking.

SUMMARY

The glass transition and crystallization temperatures of an amorphous alloy (composition in at.%: Zr–10Al–5Ti–17.9Cu–14.6Ni) are dependent upon the heating rate; the faster the heating rate, the higher the temperature. The deformation behavior of the alloy at 410°C (within the supercooled liquid region) was characterized. The alloy was found to exhibit a large tensile elongation of over 250% at a high strain rate of 10^{-2} s^{-1}. Due to structural instability it is difficult to determine the "true" strain rate sensitivity value. However, preliminary experimental results indicated that the alloy does not behave like a Newtonian fluid (m=1). This is supported by the observation that tensile samples deformed non-uniformly and exhibited macroscopic necking.

ACKNOWLEDGMENT

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