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Newtonian Flow in Bulk Amorphous Alloys

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NEWTONIAN FLOW IN BULK AMORPHOUS ALLOYS

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ABSTRACT

Bulk amorphous alloys have many unique properties, e.g., superior strength and hardness, excellent corrosion resistance, reduced sliding friction and improved wear resistance, and easy formability in a viscous state. These properties, and particularly easy formability, are expected to lead to applications in the fields of near-net-shape fabrication of structural components. Whereas large tensile ductility has generally been observed in the supercooled liquid region in metallic glasses, the exact deformation mechanism, and in particular whether such alloys deform by Newtonian viscous flow, remains a controversial issue. In this paper, existing data are analyzed and an interpretation for the apparent controversy is offered. In addition, new results obtained from an amorphous alloy (composition: Zr–10Al–5Ti–17.9Cu–14.6Ni, in at. %) are presented. Structural evolution during plastic deformation is particularly characterized. It is suggested that the appearance of non-Newtonian behavior is a result of the concurrent crystallization of the amorphous structure during deformation.

INTRODUCTION

Metallic glasses fabricated by rapid quenching from the melt were first discovered in 1960 [1]. Due to 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 10K/s. This enables the production of bulk amorphous alloys with a thickness of ~10 mm. These bulk amorphous alloys have many potential applications resulting from their unique properties, e.g., superior strength and hardness [2], excellent corrosion resistance [3], reduced sliding friction and improved wear resistance [4], and easy forming in a viscous state [5-7]. These properties, and particularly easy forming in a viscous state, should lead to applications in the fields of near-net-shape fabrication of structural/functional components.

The mechanical behavior of metallic glasses is characterized by either inhomogeneous or homogeneous deformation. Inhomogeneous deformation usually occurs when a metallic glass is deformed at low temperature (e.g. room temperature) and is characterized by the formation of localized shear bands, followed by the rapid propagation of these bands, and sudden fracture. Thus, when a metallic glass is deformed under tension it exhibits very limited macroscopic plasticity. It is pointed out that, despite a limited macroscopic plasticity, local strain within these shear bands can be, sometimes quite significant (about 10). These bands are typically 20-30 nm in width and have not yet been microscopically examined [8], although some observations indicated possible crystallization [9]. Whereas there exist many different views on inhomogeneous deformation in metallic glasses (e.g., free-volume model [10, 11] and dislocation theory [12]), there is still no universal agreement. This paper is to address only homogeneous deformation.

Homogeneous deformation in metallic glasses usually takes place at about $0.70T_g$ [11] above which metallic glasses exhibit significant plasticity. It is pointed out that 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 $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ alloy is about 533K (corresponds to $0.82T_g$) at 5×10^{-4} s^{-1}, but it is 652K (corresponds to $1.0T_g$) at 5×10^{-2} s^{-1} [6]. The strain rate dependence of T_{tr} (480–525K; 0.61–$0.75T_g$) has also been demonstrated in $Fe_{40}Ni_{40}B_{20}$ [13]. These results suggest that homogeneous deformation is associated with certain rate (or diffusional relaxation) processes. For the purpose of discussion, we divide the homogeneous deformation of metallic glasses into three regions, according to testing temperatures.

$T < T_g$

Mulder *et al* [13], in a study of the deformation of $Fe_{40}Ni_{40}B_{20}$ metallic glass in tension at elevated temperatures, found that the transition temperature from inhomogeneous to homogeneous deformation is about 480-525K (0.68–0.75 T_g), as predicted by a free volume model [11]. The also conducted creep experiments at temperatures (523–548K) below the glass transition temperature with a relatively high stress (> 1.0 GPa). Experimental results showed that the stress exponent was rather high (n=8.5). The activation energy was determined to be between 250 and 280 kJ/mol, which is similar to that for eutectic crystallization below the glass transition temperature.

Taub and Luborsky [14] also conducted tensile creep experiments on amorphous $Fe_{40}Ni_{40}P_{14}B_6$ ribbons. They found that within the temperature range of 383–582K (T_g=663K and T_x=673K, where T_x is the crystallization temperature) and at a constant tensile stress of 312 MPa the strain rate varies inversely with time but only after an initial transition. They also performed stress relaxation experiments and showed that the stress dependence of the strain rate obey a hyperbolic sine relationship (nonlinear), consistent with transition state theory [15]. To further reconcile all data, including those from the initial transition, a threshold stress (=39±4MPa) was introduced into the formulation, although the physical meaning of the threshold stress was unclear.

Most recently, Kawamura *et al* [6] studied the high-temperature deformation properties of a $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ metallic glass (T_g=652K, T_x=757K) with a wide range of ΔT (=T_g-T_x) produced by a melt spinning method. They found that, within $T_{tr}<T<T_g$, the alloy has a low strain rate sensitivity value (m<0.25) and the tensile elongation is also low (<100%). Similar observations were also made in $Pd_{40}Ni_{40}P_{20}$ metallic glasses, and results showed that at a test temperature of 560K (T_g=578-597K), the alloy exhibited a low strain rate sensitivity of only 0.20 and tensile elongation < 50%.

From the above results, we may conclude that homogeneous deformation of metallic glasses at temperatures below T_g are characterized by a low strain rate sensitivity (i.e. high stress exponent) and ductility (<100%). This is attributable to the fact that structural relaxation and recovery are still difficult as a result of sluggish diffusion in this temperature range.

$T_g < T < T_x$ (supercooled liquid region)

As early as 1980, Homer and Eberhardt [16] reported the observation of superplasticity in amorphous $Pd_{78.1}Fe_{5.1}Si_{16.8}$ ribbons (T_g=668K, T_x=683K) during non-isothermal creep experiments. In the experiments, test samples were rapidly heated to the maximum temperature of 698K under a constant load (range: 25–150 MPa). The resulted 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 698K is higher than T_x, a dispersion of 0.4 μm grains in the amorphous matrix was observed in the test samples after superplastic deformation. It is noted that slow heating during creep test resulted in the disappearance of superplasticity. This is apparently caused by easy crystallization in the alloy, as indicated by a narrow ΔT (=15K).

Zelenskiy *et al.* [17] studied the formability of amorphous $Co_{68}Fe_7Ni_{13}Si_7B_5$ (T_g=836K, T_x=856K) at temperatures between 773 and 913K. They observed large tensile ductility at a relatively fast strain rate of 10^{-2} s^{-1} within 823-853K (in the supercooled liquid region). Specifically, the maximum elongation of 180% was recorded at a corresponding minimum stress of about 150 MPa. However, strain rate sensitivity was not measured. TEM microstructural examinations indicated that 853K annealing produces nanometer grains (~50–70 nm) in the alloy. From these results, the authors argued that the presence of a large amount of grain/amorphous matrix interfacial area is necessary for the observed superplasticity. However, we want to point out that this may not be true. In fact, several experiments indicated a reduced ductility in the presence of nanograins [6, 16]. A recent study of Busch *et al* [18] also showed that the viscosity of a metallic glass increases sharply once the temperature is above the crystallization temperature. As expected, an increase in viscosity leads to an increasing resistance to plastic flow and, thus, a decrease in ductility.

To further understand superplasticity and extended plasticity in metallic glasses, Khonik and Zelenskiy [19] analyzed available mechanical data from fifteen different metallic glasses, including both metal-metal and metal-metalloid systems. They made several important observations. First, superplasticity occurs in alloys with a large ΔT, typically about several tens degrees. The larger is ΔT, the larger is 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 noticed also that a faster heating rate usually produced a larger elongation. Apparently, this is associated with structural stability since slower heating results in an earlier crystallization.

In studying the formability of a $La_{55}Al_{25}Ni_{20}$ alloy, Kawamura *et al* [7] reported that the alloy in the supercooled liquid range (480-520K) behaves like a Newtonian fluid, i.e., m=1. A tensile elongation of over 1,800% was recorded at 503K at a strain rate of 2 x 10^{-1} s^{-1}. The glassy solid below the glass transition temperature exhibited non-Newtonian viscosity, and the supercooled liquid revealed a Newtonian viscosity but changed to non-Newtonian with increasing strain rate. The elongation was reduced by the transition to non-Newtonian viscosity and crystallization. However, a careful examination of their stress-strain rate data indicated that the strain rate sensitivity tends to decrease to less than one when testing temperature (e.g. 510, 520K)

approaches T_x. Again, this is probably associated with a partial crystallization in amorphous structure during testing.

Kawamura *et al* [6] 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 were strongly dependent on strain rate and the strain rate sensitivity value exceeded 0.8, but less than one. The high strain rate sensitivity produces 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, a true Newtonian behavior (m=1) was not observed in the alloy.

To further investigate superplasticity in metallic glass systems, Kawamura *et al* [6] tested a $Pd_{40}Ni_{40}P_{20}$ alloy prepared by rapid solidification. Within 560-620K, the alloy exhibits a 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 thermally more stable than $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ in the supercooled liquid state, as pointed out by Kawamura *et al* [6]. (ΔT= 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 still retain its amorphous state, whereas crystallization may have already 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 $Zr_{65}Al_{10}Ni_{10}Cu_{15}$.

Thus, at $T_g < T < T_x$, large tensile ductility can be obtained from metallic glasses with large ΔT. The maximum ductility is expected to occur at a temperature near T_x, where the flow stress (or viscosity) is low, and high strain rates at which the alloy can retain its amorphous structure during deformation. For convenience, the above data are summarized in Table 1.

Table 1 Summary of the deformation data of some metallic glasses in the supercooled liquid region

Alloys	T_g	T_x	m	Elongation	Ref.
$Pd_{78.1}Fe_{5.1}Si_{16}$	668K	683K	~1.0	N/A	[16]
$Co_{68}Fe_7Ni_{13}Si_7B_5$	836K	856K	N/A	180	[17]
$La_{55}Al_{25}Ni_{20}$	480K	520K	1	1,800	[7]
$Zr_{65}Al_{10}Ni_{10}Cu_{15}$	652K	757K	>0.8	340	[6]
$Pd_{40}Ni_{40}P_{20}$	578–597K	651K	1.0	N/A	[6]
$Ni_{77.5}Si_{7.5}B_{15}$	N/A	N/A	1.09	N/A	[20]

$T_x < T$

At a temperature higher than T_x, metallic glass alloys are readily crystallized and form nanocrystalline structures. Whereas there are some data on plasticity of nanocrystalline solids at temperatures much greater than T_x, there exist only limited information on the mechanical behavior of metallic glasses at temperatures slightly above T_x.

Ashdown *et al* [21] studied the superplastic behavior of a crystallized Fe-Cr-Ni-B glassy alloy. By controlling crystallization, a material with a grain size of 0.2 μm was produced. Tensile elongation of over 200% was readily obtained from the material tested at strain rates of over 10^{-2} s^{-1} and at a temperature as low as 1073K; the maximum elongation of 450% was recorded at 1273K and a strain rate of 10^{-2} s^{-1}. These results are in accordance with the conventional fine-grained superplasticity.

Brandt *et al* [22] also studied the superplastic behavior of a microcrystalline (0.5 μm) $Ni_{78}Si_8B_{14}$ produced by annealing amorphous samples at 1073K. The material contains equiaxed Ni_3B and Ni_3Si grains and showed a tensile elongation of over 120% at 823–1023K. The strain rate sensitivity value was essentially constant ($m = 0.85$) over a wide range of strain rate (10^{-6} to 10^{-2} s^{-1}) and the activation energy was 72.4 kJ/mol. These results indicated the occurrence of conventional fine-grained superplasticity.

Using a similar technique, Wang and coworkers [23, 24] crystallized an amorphous $Ni_{80}P_{20}$ alloy at 603K. The crystallized alloy was nanocrystalline, consisting of 80vol% Ni_3P and 20vol% Ni. Creep experiments were subsequently conducted at 543-583K on the crystallized samples and the data showed a stress exponent of 1.2 ($m = 0.8$) and activation energy 68 kJ/mol. From these data, the authors argued that Coble creep was responsible for the deformation.

Most recently, two submicrocrystalline bulk alloys, Al–14mass% Ni–14mass% Misch Metal [25] and Mg-8.3wt%Al-8.1wt%Ga [26], were produced by the extrusion of rapidly solidified amorphous powders. The grain sizes of the extruded Al and Mg alloys were 0.1 and 0.6 μm, respectively. Resulting from fine grain sizes, both alloys were highly superplastic (elongation = 600% for Al and >1000% for Mg) and the strain rates at which superplasticity took place were also high (>10^{-2} s^{-1}).

The above experiments were all carried out at temperature much higher than T_x. In fact, the testing temperatures were sometimes close to T_m, the melting point of the alloys. At these temperatures material are no longer amorphous, but rather nanocrystalline or even microcrystalline, depending upon the thermal stability of the alloys. Conventional mechanisms for high temperature deformation, and particularly superplastic deformation, are expected to prevail.

In summary, for homogeneous deformation in metallic glasses, large tensile ductility can generally be obtained in the supercooled liquid. The exact deformation mechanism, however, and in particular whether an alloy deforms by Newtonian viscous flow or not remains a controversial issue. The purpose of this paper is to report an example of non-Newtonian behavior in a cast 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. 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 [2]. Differential scanning calorimetry was used to characterize the thermal properties of the alloy. The temperatures for the onset and end of glass transition, and the crystallization temperature (T_x), have been previously measured using differential scanning calorimetry (DSC) [27]; specifically, these temperatures are 631, 705, and 729K, respectively, at a heating rate of 20K/min.

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 Fig. 1. Tensile tests were conducted using an Instron machine equipped with an air furnace. Because of 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 a test at 683K at a constant strain rate of 10^{-2} s^{-1}, the temperature profile was: 578K (5 min), 644K (10 min), 670K (15 min), 680K (20 min), and 683 (47 min). Constant strain rate tests were performed at a constant strain rate of 10^{-2} s^{-1} with a computer-controlled machine within a temperature range of 663-743K. To measure strain rate sensitivity exponents, both strain rate cycling (i.e. cycling between 10^{-3} and 10^{-2} s^{-1}) and strain rate increase tests were performed. The amorphous nature of the alloy was confirmed using transmission electron microscopy (TEM), as shown in Fig. 2. The TEM sample was prepared by chemical milling.

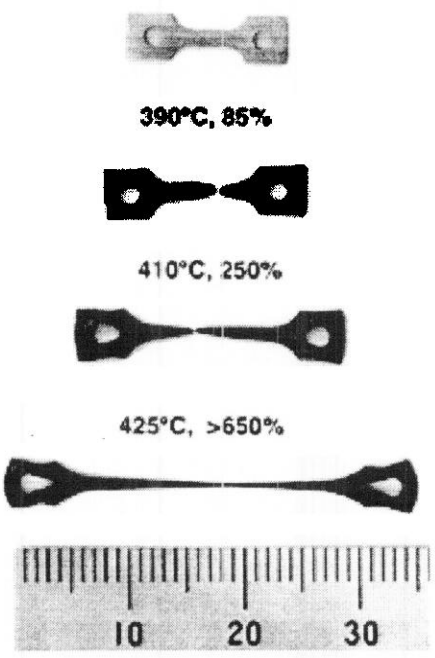
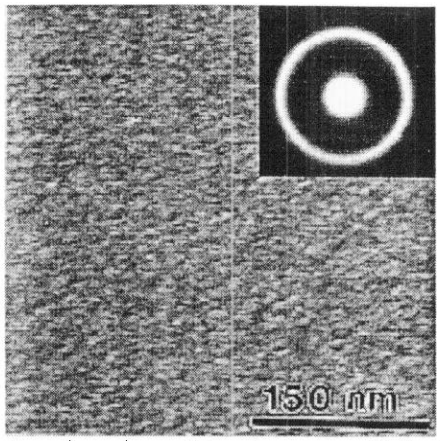


Fig. 1 Amorphous samples fractured at different temperatures. Sample necking is apparent. An untested sample is included for comparison.

RESULTS AND DISCUSSION

The stress-strain curves for the alloy at different temperatures at a strain rate of 10^{-2} s^{-1} is shown in Fig. 3. A yield drop phenomenon is readily observed at low temperatures, and in particular at 663 and 683K. In fact, at 663K the yield drop is 750 MPa (i.e. from 1600MPa to 850MPa), which is about the same magnitude as its 'normal' yield strength (~850 MPa). The yield drop phenomenon has also been observed and studied by Kawamura *et al* [5] during testing of a $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ metallic glass in the supercooled liquid region. They attributed the yield drop to a 'transient phenomenon', but the associated concurrent change of atomic structure associated with the phenomenon was not given.

It is noted that similar phenomena have also been observed in the homogeneous flow of glassy polymers and in the plastic deformation of crystalline metal alloys. In the case of glassy polymers, this behavior is associated with the stress-effected, segmental chain displacements and the preferential alignment of the long axis of the molecules along the tensile axis. Both chain displacements and molecular alignments are achievable by the nucleation and propagation of 'double kinks' along the chain axis. By contrast, in crystalline metal alloys, it



results from the locking of dislocations by solute atoms, e.g. Cottrell locking [28], or the shearing of coherent precipitates by dislocations [29]. For metallic glasses, however, neither the theory for glassy polymers or for crystalline metals appears to be applicable. Kawamura *et al* [30] argued that the yield drop was caused by an initial increase in atomic mobility at high strain rates, but, upon yielding, the atomic mobility decreases and structure relaxes. However, the exact physical process that leads to the observed yield drop is still unclear [30]. Structural clustering and chemical short range ordering are expected to impede the propagation of shear bands and may be responsible, in part, for the yield drop.

Fig. 2 Transmission electron micrograph shows the amorphous nature of the alloy.

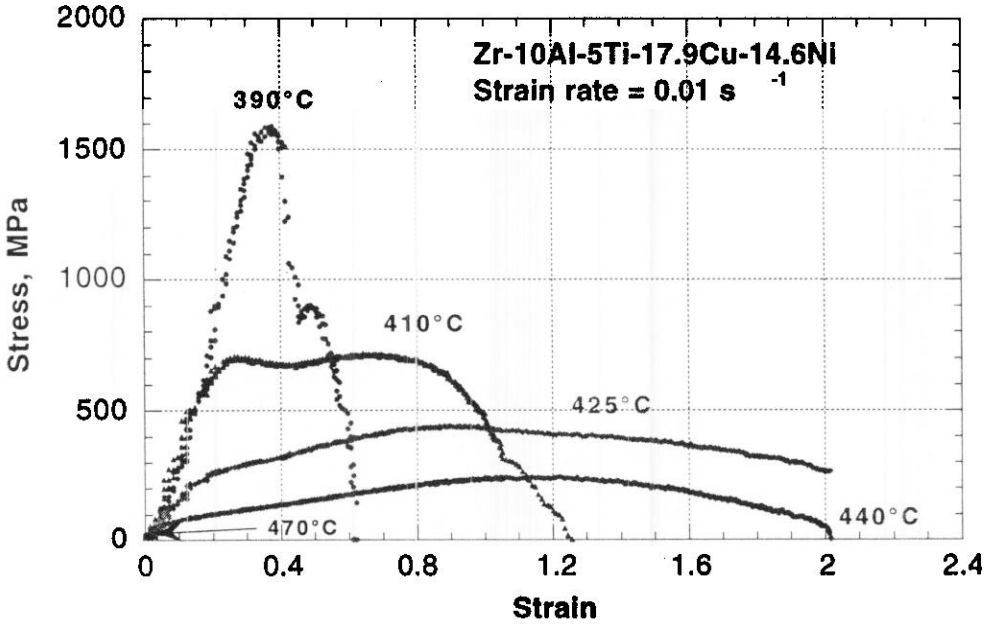


Fig. 3 Stress-strain curves of Zr-10Al-5Ti-17.9Cu-14.6Ni obtained at temperatures near the supercooled liquid region. The yield drop phenomenon is readily seen, especially at low temperatures.

The yield drop phenomenon disappears at a strain rate of 10^{-2} s^{-1} and at temperatures higher than 683K. In these temperatures, there is an initial hardening, followed by a gradual decrease in flow stress until final fracture. The fracture strain increases with increasing test temperature and reaches a maximum value of 2.0 (~650% elongation) at 698 and 713K. At 743K, which is above the crystallization temperature (729K), the alloy becomes extremely brittle; in fact, the test sample failed at the location of the loading pin. It is noted that samples, which were deformed in the supercooled liquid region, exhibit gradual necking, as shown in Fig. 2. In fact, some samples necked down nearly to a point. The final decrease in flow stress is, therefore, not a result of softening, but reduction in load bearing. This fracture appearance is different from that observed in a $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ metallic glass [5], in which uniform deformation was observed. The 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 evident in Fig. 3 that both the flow stress and fracture strain are extremely sensitive to testing temperature. For example, with only a 15K difference in testing temperature, the flow stress drops from 700MPa at 683K to about 400MPa at 698K. The tensile elongation is almost tripled (230% to 630%). The flow stresses are generally quite high; for example, at even 713K the flow stress is about 200MPa. A high flow stress was also observed in another superplastic $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ metallic glass, which was over 100MPa [6]. These values are considerably higher than the flow stresses generally observed in metals or ceramics exhibiting superplasticity or extended ductility [31]. Flow stresses for a superplastic metal or ceramic are typically lower than 35MPa. Technologically, a high flow stress can cause fast wear of the forming dies.

To characterize the deformation behavior, strain rate cycling tests were carried out at 683K to measure the strain rate sensitivity value. The result is shown in Fig. 4; the values of strain rate sensitivity m in equation $\dot{\varepsilon} = K \cdot \sigma^m$, where $\dot{\varepsilon}$ is the strain rate, σ is the flow stress, and K is a constant, were measured by strain rate cycling between 10^{-2} and 7 x 10^{-3} s^{-1}. There is no steady state region after each cycle, making it difficult to determine accurately the strain rate sensitivity value. This difficulty may be associated with structural instabilities during testing. It is noted that an external applied stress can promote crystallization in amorphous alloys [32]. Thus, despite the fact that 683K is below the crystallization temperature, it is believed that some nano-scale, crystallized phase already evolved during the course of the test. The presence of nanocrystalline phases can significantly affect the mechanical properties of a metallic glass. For example, Busch *et al* [18] 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* [33, 34] who reported that the fracture strength of an amorphous $Al_{88}Ni_{10}Y_2$ was doubled when the alloy was crystallized and contained 5-12 nm-size Al particles. Thus, in the present strain rate cycle test, 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 Fig. 4.

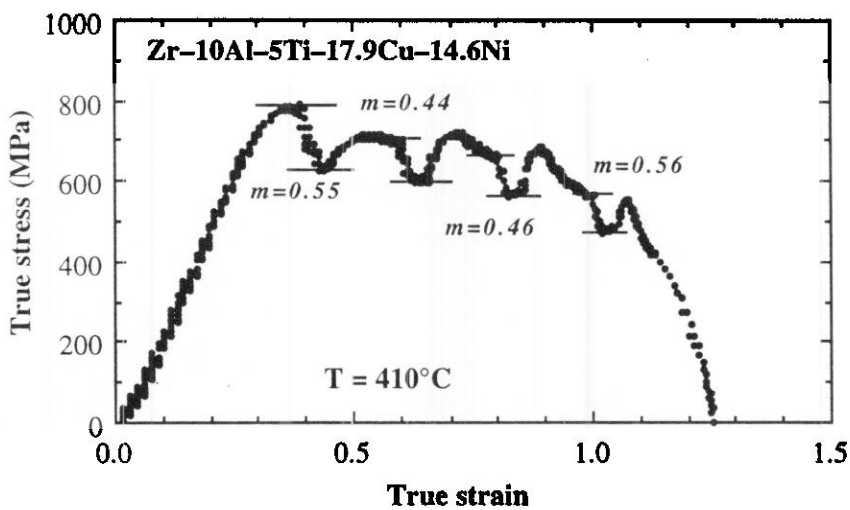


Fig. 4 Strain rate cycling test at 683K showing that the strain rate sensitivity value is only 0.45-0.55.

As shown in Fig. 4, 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 Fig. 4 indicate that the onset of sample necking occurs at a strain of approximately 0.8, which is consistent with the results observed in single-strain-rate tests (Fig. 3). The fracture obtained in the strain rate cycling test is also similar to that obtained in a constant strain rate test.

It is worth noting that from Fig. 4 the "apparent" strain rate sensitivity for the present Zr-10Al-5Ti-17.9Cu-14.6Ni 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 may be caused by the fact that the structure of the alloy in the supercooled liquid region is thermally unstable. Upon thermal exposure, and particularly under an external applied stress, the amorphous structure tends to crystallize and results in a mixture of crystalline and amorphous structure. Experimentally, it is challenging to examine the structure of a superplastically deformed specimen, primarily because tested samples necked down to nearly a point. Sample preparation for either x-ray diffraction or TEM study is, therefore, difficult. Moreover, the present experiments were performed in air, which resulted serious oxidation on test samples (see next section). The presence of a diffraction pattern may be simply indicative of oxide formation.

However, if an alloy indeed has a mixed crystalline-plus-amorphous structure, to a first approximation, the total deformation rate can be expressed by:

$$\dot{\varepsilon}_{total} = (1 - f_v) \cdot \dot{\varepsilon}_{am} + f_v \cdot \dot{\varepsilon}_{cry} \qquad (1)$$

where $\dot{\varepsilon}_{total}$ is the total strain rate, $\dot{\varepsilon}_{am}$ and $\dot{\varepsilon}_{cry}$ are the strain rates caused by the amorphous and crystalline phases, respectively, and f_v is the volume fraction of the crystalline phase. Since the plastic flow of an amorphous alloy can be described by $\dot{\varepsilon}_{am} = A\sigma$, and the plastic flow of a nanocrystalline, superplastic alloy can be described by $\dot{\varepsilon}_{cry} = B\sigma^2$, where σ is the flow stress, and A and B are material constants, Equation (1) can be rewritten as:

$$\dot{\varepsilon}_{total} = (1\text{-}f_v) \cdot A\sigma + f_v \cdot B\sigma^2 \qquad (2)$$

It is obvious that the strain rate sensitivity, which is the reciprocal of the stress exponent, would be between 0.5, the value for grain boundary sliding mechanism in fine-grained crystalline material, and unity, the value for Newtonian viscous flow.

It is interesting to comment on the drastic reduction in tensile elongation from 650% at 713K to virtually zero at 743K. A temperature of 743K is above the crystallization temperature of the alloy (~729K). At this temperature, the alloy has a nanocrystalline structure consisting of many intermetallic phases. Conventional wisdom suggests that an ultrafine grain size alloy should have a large tensile elongation, presumably resulting from extensive grain boundary sliding. However, it must be pointed out that, in the case of grain boundary sliding, 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. However, dislocation slip in an ordered, multicomponent intermetallic compound is difficult at temperatures near T_x. Also, diffusional processes are not expected to be sufficiently fast to accommodate sliding strains at strain rates of ~10^{-2} s^{-1}. This offers an explanation for a high *m* value but low tensile elongation in metallic glasses at temperatures near T_x. It is worth noting that, no accommodation is needed for pure Newtonian flow.

Microstructure and Fracture surface

Zr-based metallic glasses have poor oxidation resistance. For example, the cross-section microstructure in the vicinity of the fracture surface of the sample tested at 713K and 10^{-3} s^{-1} is shown in Fig. 5. As expected, the internal structure is featureless. However, an oxide layer, estimated to be about 4 μm thick, is present. The layer was extremely brittle and non-uniform in thickness. The uneven thickness suggests that oxide layer was fractured and new surface was continuously created, but immediately oxidized, as a result of sample stretching. The formation and fracturing of oxide layer is not expected to affect significantly the flow stress since the layer thickness is relatively low. It has also little effect on the ductility, since the material is not notch sensitive in the supercooled liquid region, except in the final stage of deformation.

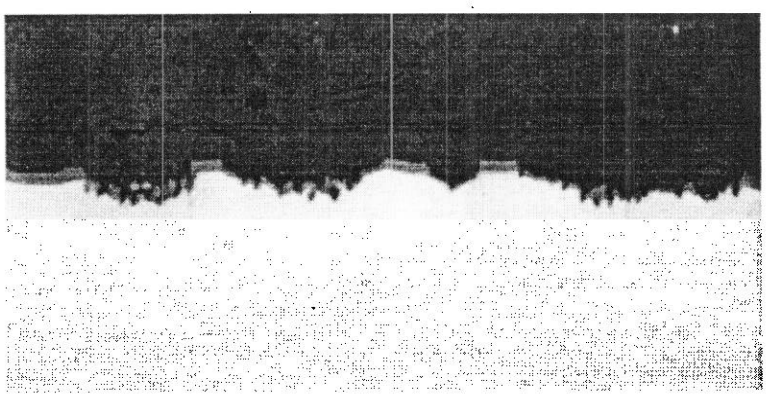


Fig. 5 Cross sectional view of the sample fractured at 713K and 10^{-3} s^{-1}. A non-uniform oxide layer is readily seen. The maximum thickness is about 4 μm.

It is well known that, at room temperature, the fracture surface of a metallic glass exhibits a vein pattern (Fig. 6), as a result of the sudden release of elastic energy at fracture [2]. Also, sample does not show any necking after fracturing. These are typical fracture characteristics for metallic glasses deformed inhomogeneously. In contrast, metallic glasses show strong resistance to necking in the supercooled liquid region; this is readily observed in Fig. 1. The strong necking resistance is apparently a result of high strain rate sensitivity.

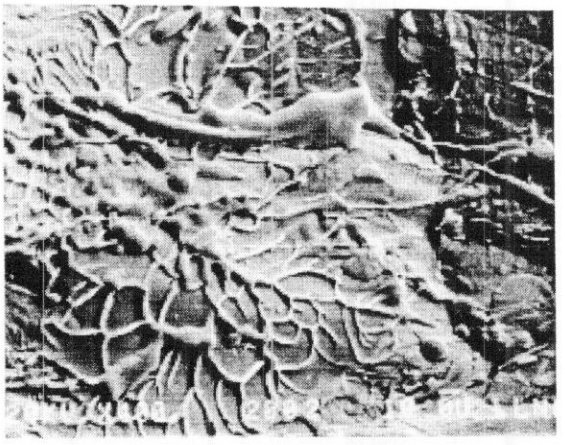


Fig. 6 Vein pattern formed on the fracture surface of amorphous of Zr-10Al-5Ti-17.9Cu-14.6Ni tested in tension at room temperature. Melted droplets are readily seen.

The fracture surface of the sample tested at 663K and at a strain rate of 10^{-2} s^{-1} is shown in Fig. 7. It appears that vein pattern persists even at 663K, where homogeneous deformation prevails. However, a close examination of Fig. 7 indicates that the pattern is actually different from that observed at room temperature. Specifically, the ridges between voids are much higher and there is no indication of melting. In addition, large voids were present. These voids were obviously developed prior to the final fracture of the sample; they were formed under a triaxial stress. As shown in Fig. 1, the sample exhibits considerable necking. The reduction in area for the 663K sample was about 96%. At 683K sample fractured nearly to a chisel point (reduction in area>99%). The fracture surface, as shown in Fig. 8, reveals a ductile dimple fracture with the absence of vein pattern. The brittle-to-ductile transition from inhomogeneous to homogeneous deformation is clearly revealed by the fracture surface appearance.

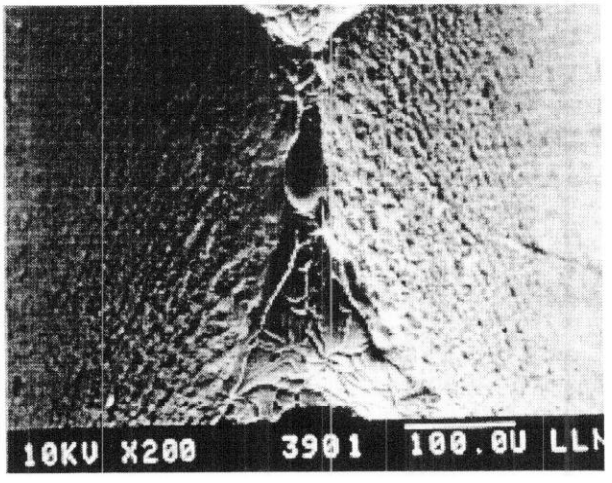


Fig. 7 Fracture surface of the sample tested at 663K and at a strain rate of 10^{-2} s^{-1}.

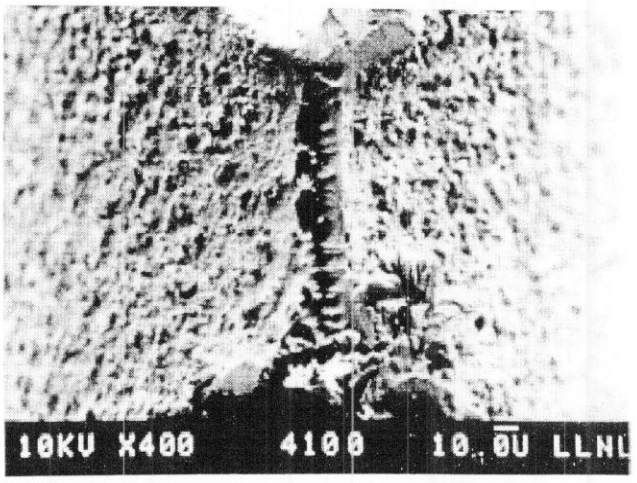


Fig. 8 Fracture surface of the sample tested at 683K and at a strain rate of 10^{-2} s^{-1} reveals a ductile dimple appearance with the absence of vein pattern.

SUMMARY

The deformation behavior of a Zr–10Al–5Ti–17.9Cu–14.6Ni metallic glass was characterized in the supercooled liquid region. The alloy was observed to exhibit a large tensile elongation in this region; a maximum tensile elongation of over 600% was recorded at 698-713K at a high strain rate of 10^{-2} s^{-1}. The superplastic properties, e.g. flow stress and elongation, are found to be very sensitive to testing temperature. As a result of structural instabilities it is difficult to determine the "true" strain rate sensitivity value. Despite this difficulty, experimental results indicated that the alloy does not behave like a Newtonian fluid (m=1). It is suggested that the non-Newtonian behavior is caused by the concurrent crystallization of the amorphous structure during deformation; a mixed crystalline-plus-amorphous structure was actually tested. At temperatures above the crystallization temperature, in spite of having a nanocrystalline structure, the alloy exhibit limited ductility. This is a result of poor strain accommodation at grain triple junctions. Microstructural examination of the fracture sample is now underway.

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