PRACE INSTYTUTU ODLEWNICTWA
TRANSACTIONS OF FOUNDRY RESEARCH INSTITUTE

Volume LVII Year 2017 Number 4

Viscous flow features of amorphous $Zr_{65}(Ni,Pd)_{35}$ alloy

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Received: 11.10.2017. Accepted in revised form: 29.12.2017.

DOI: 10.7356/iod.2017.33

Abstract

Viscous flow behavior of amorphous $Zr_{65}(Ni,Pd)_{35}$ alloy has been studied at a heating rate of 20 K/min. The viscosity experimental results are interpreted on the basis of the free volume model. The values of the model parameters obtained are used for estimation of glass forming ability in terms of the Angell parameter, and the fracture strength of the alloys based on its correlation with the glass transition temperature.

The glass transition temperature is 663 K. The alloy $Zr_{65}(Ni,Pd)_{35}$ possesses excellent fracture strength of about 2.28 GPa, comparable to that of stainless steels.

The relatively good thermal and excellent mechanical properties make this alloy promising for preparing bulk amorphous samples.

Keywords: *metallic glass, viscosity, glass-forming ability*

1. Introduction

Zr-based amorphous metal alloys have a good combination of excellent mechanical properties, excellent corrosion resistance and a low coefficient of thermal expansion [1–4]. The main reasons for extensive research in the field of these alloys are:

– Ability to form metal-metal glass;

– Ability to form glass in a wide range of compositions [5–7];

– Specific glass-crystal transition – some of the Zr-based metallic glasses crystallize in phases of the same composition [8].

The importance of Zr-Ni, Zr-Co, Zr-Fe, Zr-Cu and Zr-Cr systems, which are very common, is determined on one hand by the fact that rapid solidification enables amorphous alloys to be formed in a large range of compositions and, on the other hand, to develop on their basis a significant number of multi-compartmental metal glasses which, when rapidly cooled, can form massive ingots [9,10].

The aim of this work is to investigate the viscous flow behavior of amorphous alloy $Zr_{65}(Ni,Pd)_{35}$.

2. Theoretical background

The temperature dependence of the viscosity of amorphous metal alloys under non-isothermal conditions can be interpreted on the basis of the Free Volume Model (FVM) with one general dependence [11]:

$$\eta = \eta_0 T \exp\left(\frac{Q_\eta}{RT}\right).\frac{1}{c_f} \qquad (1)$$

Here Q_η is the activation energy for the viscous flow, η_0 is a pre-exponential factor and c_f is the concentration of flow defects. The equilibrium concentration of flow defects $c_{f,eq}(T)$ is given by $c_{f,eq}(T) = \exp(-B/(T - T_o))$ where B and T_0 are two model parameters which can be related to the empirical constants B_{VFT} and $T_{0,VFT}$ in the classical empirical Vogel-Fulcher-Tammann equation. Replacing $c_{f,eq}(T)$ in Equation (1) the so-called "hybrid" temperature dependence of quasi-equilibrium viscosity η_{eq} is obtained:

$$\eta_{eq}(T) = \eta_0 T \exp\left(\frac{Q_\eta}{RT}\right).\exp\left(\frac{B}{T-T_0}\right) \qquad (2)$$

Equation (2) describes the change of viscosity of glass forming undercooled (metallic) melts in the structural state, where the flow defect concentration follows immediately the changes of temperature. Russew et al. proposed an equation of Bernoulli of the 2nd order [12,13] describing the change of c_f in the glassy alloy with temperatures under non-isothermal conditions and at a constant heating rate q in the temperature range around the glass transition temperature:

$$c^{-1}{}_f = \left[c^{-1}{}_{f,0} - \int_{T_o}^{T} Q(T') \exp\left(- \int_{T_o}^{T'} P(T'') dT'' \right) dT' \right] \exp\left(\int_{T_o}^{T} P(T') dT' \right) \quad (3)$$

where $P(T) = -\frac{\nu_r}{q} \exp\left(-\frac{Q_r}{RT} - \frac{B}{T - T_0} \right)$,

and $Q(T) = -\frac{\nu_r}{q} \exp\left(-\frac{Q_r}{RT} \right)$;

ν_r is the attempt frequency,

Q_r is activation energy of relaxation,

$c_{f,0}$ is the initial defect concentration

and R is the universal gas constant.

Combining Equation (1) with Equation (3), one obtains the temperature dependence of viscosity η in the high temperature range near T_g. The Free Volume Model interpretation of the viscosity experimental data allows specifying the model parameters in Equation (1) and Equation (3) by using multi-parameter regression analysis.

2.1. Glass Forming Ability (GFA) and Melt Fragility Number

Angell [14] classifies the glass forming melts as "strong" and "fragile" depending on their viscosity temperature dependence in coordinates log10(η) vs. T_g/T. The slope of this temperature dependence at T_g/T = 1 defines the so-called melt fragility number of Angell m_A. The higher the m_A, the more fragile the liquid and vice versa. In the physics of amorphous bodies, fragility characterizes how rapidly the dynamics of a material slow down as it is cooled toward the glass transition temperature T_g. Materials with a higher fragility have a relatively narrow glass transition temperature range, while those with low fragility have a relatively broad glass transition temperature range. Liquids of Arrhenius-type are described as "strong," and these of Vogel-Fulcher-Tammann type as "fragile." The strong liquids possess a melt fragility number m_A lower than 10, while the "fragile" liquids have melt fragility numbers about 100 or more. Metallic glasses occupy an intermediate position with melt fragility numbers between 30 and 60. The higher the melt fragility number of Angell, the lower is the glass forming ability of metallic melts. The melt fragility number of Angell can be conveniently used as a measure for GFA.

According to the approach proposed by Angell [14], available data on the viscosity of the supercooled metal melt is presented as a function of T_g/T. The slope of the curve at T_g presents the melt fragility number of Angell m_A:

$$m_A = \left[\frac{d(\log \eta)}{d\left(\frac{T_g}{T} \right)} \right]_{T=T_g} \quad (4)$$

Equation (4) is based on the assumption that melt viscosity of glass forming substances follows Vogel-Fulcher-Tammann temperature dependence. In the case of FVM interpretation the viscosity temperature dependence should be presented by the "hybrid" Equation (2) instead of Vogel-Fulcher-Tammann-type equation. In this case:

$$m_A = 0.434 \left[\frac{BT_g}{(T_g - T_o)^2} + \frac{Q_\eta}{RT_g} - 1 \right] \quad (5)$$

2.2. Fracture strength

Yang et al. [15] make a successful attempt to bring dependence on the strength of metallic glasses based on the physical analogy between plastic deformation and the glass transition process. As a result, they come to the interesting and important conclusion that the fracture strength at room temperature can be predicted by the glass transition temperature T_g and the molar volume V_m (of a mixture of components) by a simple dependence:

$$\sigma_f = 55 \frac{(T_g - T_{room})}{V} \quad (6)$$

3. Experimental procedure

The ternary Zr-Ni-Pd master alloy was prepared by arc melting the mixture of the pure metals (Pd 99.8, Ni 99.95, and Zr 99.95) under argon atmosphere. Amorphous ribbons are produced by melt-spinning under helium atmosphere of 300 mbar, using a quartz crucible and a copper quenching wheel with a diameter of 250 mm and a surface velocity of 35 m.s^{-1}. The dimensions of the ribbons range from 1.08 to 1.12 mm in width and ~40 mμ in thickness.

The microstructure of the as-cast and annealed alloys was characterized by X-ray diffraction (XRD) with CuKα radiation. The viscous behavior of the amorphous ribbon in heating mode at 20 K/min was studied using the Perkin Elmer quartz thermomechanical TMS2 analyzer.

4. Results and discussion

4.1. Thermo-mechanical analysis

Typical experimental elongation-temperature (time) curves of $Zr_{65}(Ni,Pd)_{35}$ glassy alloy at 20 K/min are shown in Figure 1.

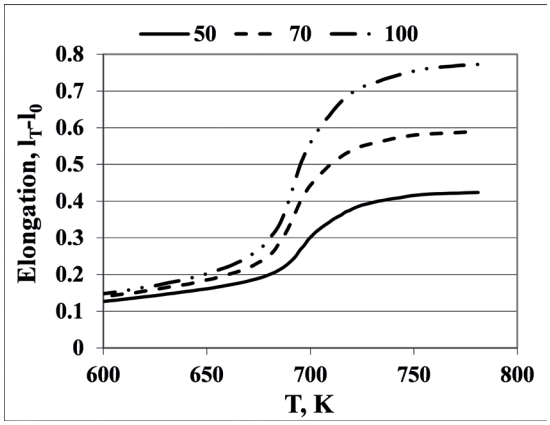

Fig. 1. Experimental elongation temperature curves $[l_T - l_0]$ of $Zr_{65}(Ni,Pd)_{35}$ glassy alloy at a heating rate of 20 K/min. The applied loads were 0.05, 0.7 and 0.1 kg respectively

The overall strain of a glassy alloy ribbon reached at temperature T under applied tensile stress and continuous heating conditions can be presented as:

$$\varepsilon(T) = [l(T) - l_0]/l_0 = \varepsilon_\sigma^{el}(T) + \varepsilon_\sigma^{an}(T) + \varepsilon_\sigma^{rel}(T) + \varepsilon_\sigma^{te}(T) + \varepsilon_\sigma^{vf}(T), \quad (7)$$

where l_0 and $l(T)$ are the initial length and the current length of the specimen at temperature T respectively, $\varepsilon_\sigma^{el}(T) = \sigma/E(T)$ represents the elastic strain of the ribbon, with $E(T)$ – the Young's modulus of the material, and $\varepsilon_\sigma^{an}(T)$ represents the possible anelastic contribution to the overall strain, $\varepsilon_\sigma^{rel}(T)$ takes into account the contribution of any relaxation effects to the overall strain, $\varepsilon_\sigma^{te}(T)$ represents the contribution of the thermal expansion to the overall strain, and $\varepsilon_\sigma^{vf}(T)$ takes into account the contribution of viscous flow to the overall strain, respectively.

The following considerations can be made with respect to the different strain contributions. The temperature dependence of Young's modulus $E(T)$ is very weak. This is a common feature for Young's modulus of metals and alloys at temperatures much lower than their melting point. As the maximal absolute values of the stresses by our creep experiments do not usually exceed 15 MPa, the magnitude of the elastic strain contribution to the overall strain is estimated to be lower than 1×10^{-4} in most cases, and thus can be neglected. The anelastic contribution $\varepsilon_\sigma^{an}(T)$ to the overall strain almost certainly cannot be neglected at lower temperatures. The first approximation of $\varepsilon_\sigma^{an}(T)$ in the temperature range $(T_g - 50\ K) \div T_g$ could be neglected. They have shown unambiguously that in the temperature range $(T_g - 100\ K)$ the anelastic deformation contribution to the overall strain can be neglected. Since the coefficient of thermal expansion and the rate of relaxation are independent of stress, the strain contributions $\varepsilon_\sigma^{te}(T)$ and $\varepsilon_\sigma^{rel}(T)$ to the overall strain $\varepsilon_\sigma^{an}(T)$ of a ribbon tested under conditions differing only in the applied tensile stresses $\sigma_1(T)$ and $\sigma_2(T)$ should be equal. Taking into account these considerations one obtains:

$$\Delta\varepsilon_{1,2}(T) = \varepsilon_{\sigma 1}(T) - \varepsilon_{\sigma 2}(T) \cong \varepsilon_{\sigma 1}^{vf}(T) - \varepsilon_{\sigma 2}^{vf}(T), \quad (8)$$

where $\Delta\varepsilon_{1,2}(T)$ is caused by an effective stress $\Delta\sigma_{1,2} = \sigma_1 - \sigma_2$.

The determination of temperature dependence of viscosity around the glass transition temperature can be followed in detail using the experimental results presented in Figures 2–5.

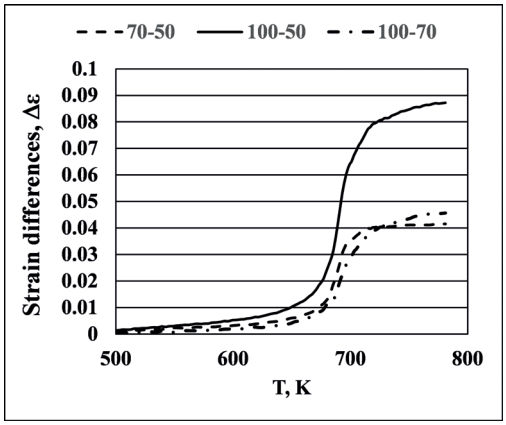

Fig. 2. Temperature dependences of strain differences Δε for the $Zr_{65}(Ni,Pd)_{35}$ glassy alloy at a heating rate of 20 K/min: $\Delta\varepsilon_{70-50} = \varepsilon_{70} - \varepsilon_{50}$; $\Delta\varepsilon_{100-50} = \varepsilon_{100} - \varepsilon_{50}$; $\Delta\varepsilon_{100-50} = \varepsilon_{100} - \varepsilon_{50}$ which are caused by applied effective loads of 0.05; 0.07; and 0.1 kg

Figure 2 shows the temperature dependences of strain differences $\Delta\varepsilon$ for the $Zr_{65}(Ni,Pd)_{35}$ glassy alloy at a heating rate 20 K/min, which are caused by applied effective loads of 0.05, 0.07 and 0.1 kg.

The typical temperature dependence of the strain rate $\Delta\dot{\varepsilon}(T)$ caused by shear stress differences $\Delta\tau_{1-2} = \frac{1}{3}(\sigma_1 - \sigma_2)$ are shown in Figure 3. That curve is obtained by numerical differentiation of the curve shown in Figure 2. The strain rate increases smoothly up to approximately 687 K where a crystallization peak is observed, Figure 3. On reaching this temperature,

a rapid increase in the strain rates is observed as a result of reaching T_g of the alloy studied.

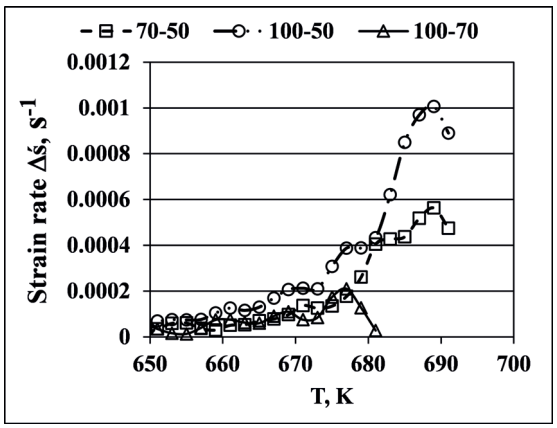

Fig. 3. Temperature dependence of the strain rates of the amorphous glassy alloy $Zr_{65}(Ni,Pd)_{35}$ at a heating rate of 20 K/min: □ – $\Delta\dot{\varepsilon}_{70-50}(T)$ and Δ – $\Delta\dot{\varepsilon}_{100-50}(T)$

Figure 4 shows the shear viscosity (line) calculated by the strain rate in Figure 3. The points represent a smooth curve of all viscosity data. A common feature of the viscosity curves obtained by measuring under a constant heating rate is the presence of two almost linear parts and curved transitional portion between them. The steeper part of the temperature dependence represents the approaching of the quasi-equilibrium structural state of under-cooled liquid of the alloy, described by the "hybrid" equation (3). The other one in the lower temperature region is the non-equilibrium viscosity of the vitrified alloy. In the temperature range of initial crystallization, the viscosity values are influenced by the increasing volume fraction of crystallized regions.

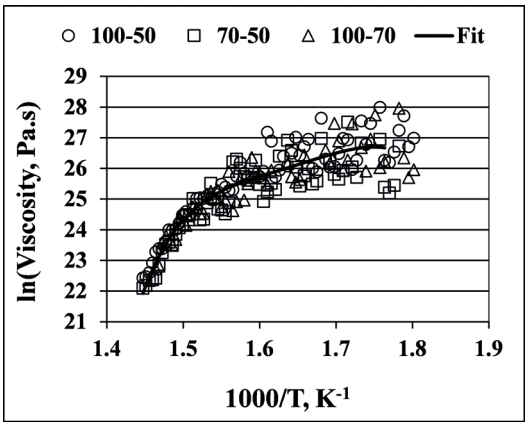

Fig. 4. Viscosity temperature dependence of $Zr_{65}(Ni,Pd)_{35}$ glassy alloy at a heating rate of 20 K/min. The solid line (−) represents the best fit curve of all data, obtained at different load differences

Figure 5 presents the measured (points) and calculated (curves) according to the free volume model temperature dependencies of the viscosity η of the $Zr_{65}(Ni,Pd)_{35}$ alloy at 20 K/min. A combination of equations (1) and (3) is used for obtaining the non-equilibrium viscosity curves and equation (3) for the quasi-equilibrium viscosity curves (steeper curve in Fig. 5).

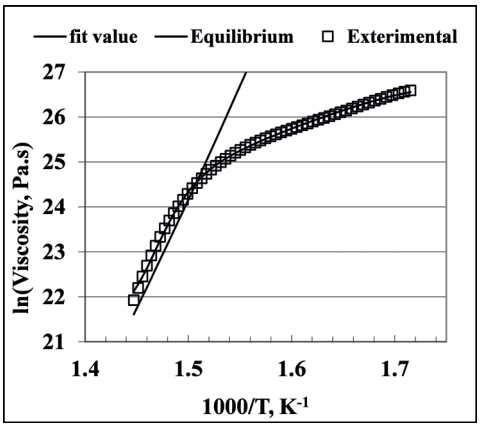

Fig. 5. Viscosity temperature dependence of $Zr_{65}(Ni,Pd)_{35}$ glassy alloy at a heating rate of 20 K/min: □ – experimental values; solid line – best fit values (−) according to Equation (1); and steep solid line – quasi-equilibrium viscosity (−) according to Equation (3), obtained by varying of free volume model parameters B, T_0, Q_η, Q_r, $c_{f,0}$, η_0 and v

The glass transition temperature, T_g and the value of the viscosity at T_g, $\eta(T_g)$, the values of the model parameters in Equations (1−3), v_r, Q_r, $c_{f,0}$, T_0, Q_η, B and η_0, obtained by regression analysis of the experimental data are given in Table 1.

Table 1. Best fit FVM parameters, experimentally determined glass transition temperature T_g, Angel's fragility number m_A and estimated according Yang fracture strength of the studied alloy

Parameters	Dimension	20 K/min
n	1/s	2.36E+15
Q_r	J/mol	120000
$c_{f,o}$		4.21E-06
R	J/molK	8.31451
T_o	K	390
dT	K	0.25
Qh	J/mol	210201
η_0	Pa s/K	3.1901E-16
$\eta(T_g)$	Pa s	4.12E+10
m_A	–	32
σ	GPa	2.28

Using the FVM parameters from Table 1 the fragility number, and the fracture strength, could be estimated using the Equations (5) and (6). The obtained values are shown in the two last rows of Table 1.

5. Conclusions

The glass transition temperature is 663 K. The alloy $Zr_{65}(Ni,Pd)_{35}$ possesses excellent fracture strength of about 2.28 GPa, comparable to that of stainless steels.

The relatively good thermal and excellent mechanical properties make this alloy promising for preparing bulk amorphous samples.

Acknowledgments

The results were obtained with the financial support of the NSF of Bulgaria project No. ДН 07/17/15.12.16 entitled “New approach for structure and properties design of amorphous and nanocrystalline metallic foams” funded by the Fund “Scientific Research” of Bulgaria.

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