Arrhenius activation of $\text{Zr}_{65}\text{Cu}_{18}\text{Ni}_7\text{Al}_{10}$ bulk metallic glass in the supercooled liquid region

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Abstract

In the current research, the dynamic mechanical spectrum and compressive deformation of $\text{Zr}_{65}\text{Cu}_{18}\text{Ni}_7\text{Al}_{10}$ bulk metallic glass in the supercooled liquid region (SLR) are investigated. The experimental results prove the existence of transition from Newtonian flow to non-Newtonian flow in the metallic glasses. In addition, we found that the characteristic stress σ_{tc} , which is obtained by a stretched exponential function based on the normalized viscosity, can be regarded as a transition point from Newtonian to non-Newtonian flow. The correlation between strain rate sensitivity exponent and corresponding strain rate was obtained at a certain temperature. It is noted that the variation of transition strain rate from Newtonian to non-Newtonian flow with different absolute temperatures follows the Arrhenius equation. The activation energy is in good accordance with that using the mechanical spectroscopy method.

Keywords: A. Metallic glass, B. Mechanical properties, B. Superplasticity, C. viscosity, F. mechanical testing

1. Introduction

Metallic glasses show special performance, such as high elastic limit strength, hardness, high fracture toughness and excellent corrosion resistance [1-3]. However, researches on mechanical behaviors of bulk metallic glasses indicated that most of bulk metallic glasses exhibit poor plasticity at room temperature [4-6]. If metallic glasses with specific components were observed to have good plastic deformation in the compression test, nucleation and propagation of the shear bands would be formed all over the surface of the sample [7-9]. Many investigations demonstrated that homogeneous deformation occurred at above $0.8 T_g$ (the glass transition temperature), which presents pronounced plasticity [10-13]. At high strain rates or low temperatures, the apparent viscosity decreases in compression with increasing of strain rate, and the glass exhibits Newtonian fluid behavior with the increase of temperature or decrease of strain rate [10-14]. In the homogeneous flow, the transition behaviors from Newtonian to non-Newtonian flow in the supercooled liquid region have been investigated for Pd-and Zr-based metallic glasses under constant strain-rate compression [14-18]. A master curve of the normalized viscosity η/η_N versus $\dot{\epsilon} \cdot \eta_N$ at different temperatures can be obtained by using the stretched exponential function, but the physical meaning of fitting parameters still remains unclear and requires further research. More importantly, although the Newtonian viscosity can be calculated at a certain temperature [14-17], the transition strain rate from Newtonian to non-Newtonian flow is not clear at a certain temperature, and it is not yet understand how the transition strain rate changes with temperature.

In the current research, the $Zr_{65}Cu_{18}Ni_7Al_{10}$ (in atomic %) metallic glass was

selected [19]. First of all, dynamic mechanical experiments of bulk metallic glasses were conducted. The apparent activation energy of the main relaxation, which corresponds to the dynamic glass transition, could be described by the classical Arrhenius equation. In parallel, compressive experiments were carried out in the supercooled liquid region. The Newtonian viscosity at different temperatures as well as the strain rate sensitivity exponent at fixed strain rate could be obtained. The transition strain rate from Newtonian to non-Newtonian is displayed at a certain temperature, and the variation of transition strain rate with different absolute temperatures satisfies the Arrhenius empiric equation. It is noted that the activation energy in the supercooled liquid region obtained by different experimental methods are in good agreement with each other.

2. Experimental procedure

The Zr-based metallic glasses were prepared by copper mould suction casting technology in Ti-gathered high purity Ar atmosphere. The cylindrical samples with a diameter of 3 mm were prepared for compression tests. The plate specimens were used for the dynamic mechanical experimental analysis in the current research. X-ray diffraction (XRD, Philips PW3830) experiments were performed to characterize the amorphous nature by using the monochromatic Cu-K α radiation at ambient temperature. The glass transition and crystallization behaviors were carried out in high purity dry nitrogen flow by using a standard commercial differential scanning calorimetry (DSC, NETZSCH DSC 200F3) at a heating rate of 20 K/min. To ensure the reliability and accuracy of the experimental data, the temperature was calibrated by the standard specimens, indium and zinc, prior to the experiments.

Dynamic mechanical measurements of bulk metallic glasses were carried out in a commercial Dynamic Mechanical Analysis (DMA, TA DMA Q800). Experiments were conducted by setting a sinusoidal shear strain (20 μm) as an excitation signal, at a fixed frequency (ranging from 0.1 to 1 Hz) with a continuous and constant heating rate of 3 K/min. Experimental samples with the dimensions of approximate 30mm (length) $\times$ 2 mm (width) $\times$ 1 mm (thickness) were prepared by low speed precision cutting machine. In order to ensure the reliability of experimental data, all the surfaces of each sample were polished to assure regularity. The experiments were performed in various nitrogen flows to ensure a certain strain (or stress) with the application of air bearing. A periodic shear strain was applied and the corresponding stress was measured simultaneously. Therefore, the complex modulus ($E^* = E' + iE''$) could be deduced and both storage modulus (E') and loss modulus (E'') can be calculated.

High temperature compression samples with a diameter of 3 mm and height of 5 mm were cut from as-cast rods. Prior to the experiments, both ends were polished carefully by diamond paste to ensure dustless and perpendicular to the compressive direction. A series of uniaxial compressive tests were conducted by using a Zwick/Roell Z020 mechanical testing system equipped with a heating furnace. The experiments were performed by means of strain rate jumps at the temperature of 643 K, 653 K, and 663 K, respectively, which fall within the ranges of supercooled liquid region (SLR). The temperature of furnace was heated to the target temperature for 30 min, the sample was then set into the furnace. The compressive experiments were conducted by keeping the temperature stable for 5 minutes. The strain rate interval was from 1×10^{-4} to $5 \times 10^{-3} \text{ s}^{-1}$.

3. Experimental Results

The XRD pattern of the $\text{Zr}_{65}\text{Cu}_{18}\text{Ni}_7\text{Al}_{10}$ bulk metallic glass after performing experiment at 663K is presented in Fig. 1. The amorphous structure of the $\text{Zr}_{65}\text{Cu}_{18}\text{Ni}_7\text{Al}_{10}$ bulk metallic glasses can be verified in the process of experiment.

As shown in Fig. 2, a typical DSC curve was conducted at a heating rate of 20K/min, and the glass transition temperature $T_g = 643$ K and temperature of the onset of crystallization $T_x = 757$ K were obtained from the DSC line chart. The experimental results agree well with the previously published data [19]. The DSC traces exhibit one single endothermic event, which represents the characteristic of glass transition, followed by an exothermic reactions corresponding to a crystallization process of the supercooled liquid.

To understand atomic mobility of the amorphous alloys, dynamic mechanical analysis was conducted at the heating rate of 3 K/min with fixed frequencies of 0.1 Hz, 0.3 Hz, and 1Hz, respectively. The normalized loss modulus E''/E_u of the $\text{Zr}_{65}\text{Cu}_{18}\text{Ni}_7\text{Al}_{10}$ bulk metallic glass obtained from loss modulus divide by storage modulus at room temperature E_u are given in Fig. 3. As shown in the figure, with increasing temperatures, there exists an obvious peak on each curve, which corresponds to the main or α relaxation. It can be observed that T_α is close to T_g as expected. The subtle difference comes from the fact that both T_α and T_g are sensitive to the heating rate. The temperature corresponding to the peak of normalized loss module increases gradually along with higher excitation frequency, which reflects the characteristics of dynamic glass transition and denotes the dynamic characteristics of main relaxation. At the specified operation frequency, α relaxation process obeys the

Arrhenius law between the excitation frequency and the absolute temperature corresponding to the peak of normalized loss module [20,21]:

$$\omega_{\max} = \omega_0 \exp\left(-\frac{E_\alpha}{kT}\right) \quad (1)$$

where $\omega_{\max}$ is the excitation frequency at certain curves, and ω_0 is a pre-exponential frequency. k is the Boltzmann constant, and E_α is the apparent activation energy of α relaxation. As illustrated in the insert of Fig. 3, at a continuous heating rate of 3 K/min, the excitation frequency shows linearly correlation to the reciprocal of temperature corresponding to the maximum normalized loss modulus. For the studied bulk metallic glasses, the apparent activation energy of α relaxation E_α was estimated close to 4.59 ± 0.09 eV. This value is in reasonable agreement with other Zr-based bulk metallic glasses, which was estimated to be as high as 5.5 eV [21].

Fig. 4 displays a typical true compressive stress-strain curve of the $\text{Zr}_{65}\text{Cu}_{18}\text{Ni}_7\text{Al}_{10}$ bulk metallic glass under strain rate jump tests from 1×10^{-4} to $2.5 \times 10^{-3} \text{ s}^{-1}$ at 643K. It clearly shows that the steady state flow stress increases with the stain rate. In the compressive strain rate jump tests, the apparent viscosity η of metallic glasses can be described as [16]:

$$\eta = \frac{\sigma_f}{3 \dot{\varepsilon}} \quad (2)$$

where σ_f is the steady state flow stress and $\dot{\varepsilon}$ is the corresponding strain rate. As shown in Fig. 5, the change of apparent viscosity η was obtained at various temperatures, which is depending on the strain rate. As reported in previous researches [15-17], a non-Newtonian behavior, which is characterized by the viscosity dependent on strain rate, is observed at lower temperature or at higher strain rate of

quasi-static compression. At higher temperature or lower strain rate, a Newtonian behavior appears with the viscosity independent of strain rate.

4. Discussion

4.1 Activation Volume

It is well known that the free volume plays a prominent role in the mechanical properties of bulk metallic glasses [22-24]. According to the free volume theory, the compressive strain rate at high temperature of metallic glasses can be described as [23]:

$$\dot{\varepsilon} = 2c_f \nu_D \exp\left(-\frac{\Delta G^m}{kT}\right) \sinh\left(\frac{\sigma_f V}{2\sqrt{3}kT}\right) = \dot{\varepsilon}_0 \sinh\left(\frac{\sigma_f V}{2\sqrt{3}kT}\right) \quad (3)$$

where $\dot{\varepsilon}_0(c_f) = 2c_f \nu_D \exp(-\Delta G^m/kT)$ is the frequency factor and can be regarded as a constant at a certain temperature, ν_D is the Debye frequency, ΔG^m is the appear activation energy, V is the activation volume defined as the volume of matter involved in each elementary defect jump, σ_f is the steady state flow stress, k is the Boltzmann constant, T is the absolute temperature and c_f is the concentration of the flow defects.

As shown in Fig. 6, the steady state flow stress changes with the applied strain rate of $\text{Zr}_{65}\text{Cu}_{18}\text{Ni}_7\text{Al}_{10}$ metallic glass, which can be described by Eq. (3) at high temperature with homogenous deformation. The activation volume V and the strain rate factor $\dot{\varepsilon}_0$ can be obtained simultaneously, as list in Table I. The activation volume in the homogenous deformation is about 0.217 nm^3 around T_g , which is consistent with previous studies on Zr-based metallic glasses, as shown in Table II. Assuming that the average atomic volume of $\text{Zr}_{65}\text{Cu}_{18}\text{Ni}_7\text{Al}_{10}$ metallic glass is $\Omega = 0.013 \text{ nm}^3$ [30], it represents that about 17 atomic volumes participate in a certain

activation process. In our former research on creep of the $\text{Zr}_{65}\text{Cu}_{18}\text{Ni}_7\text{Al}_{10}$ metallic glass [19], the activation volume is in the vicinity of 0.12 nm^3 and corresponding to about 10 atoms, which is because the test temperature are slightly lower than T_g . Another reason could be from different force types. The strain rate jump inclines to active motion organization, while creep refers to a relatively passive activation process of atomic clusters.

In addition, an Arrhenius relationship exists between frequency factor and absolute temperature:

$$\dot{\varepsilon}_0 = \varepsilon_0 \exp\left(-\frac{Q_{app}}{kT}\right) \quad (4)$$

where A_0 is a frequency constant, k is the Boltzmann constant, Q_{app} is the appear activation energy to overcome the barrier. Fig. 7 illustrates an Arrhenius plot of Frequency factor $\dot{\varepsilon}_0$ versus the reciprocal of temperature. The apparent activation energy obtained from the fitting straight line in Fig. 7 is $5.28 \pm 0.05 \text{ eV}$, which is in good correspondence to that of $\text{Zr}_{63.36}\text{Cu}_{14.52}\text{Ni}_{10.12}\text{Al}_{12}$ (5.2 eV) [31].

4.2 Viscosity

At relatively low temperature, the plastic deformation of metallic glass is usually inhomogeneous and related to deformation of the localized shear bands, followed by the propagation on shear bands [7, 32]. At high temperature above 0.8 times of T_g , homogeneous deformation could occur in metallic glasses and exhibits a significant plastic deformation [15, 20, 24]. With the high temperature deformation, there appears a transition from Newtonian to non-Newtonian viscous flow with the increase of temperature as well as the decrease of strain rate [33, 34].

In the high temperature compression test, the viscosity of the glassy materials can

be expressed as:

$$\eta = \frac{\sigma_f}{3\dot{\varepsilon}} = \frac{\sigma_f}{3\dot{\varepsilon}_0 \sinh\left(\frac{\sigma_f V}{2\sqrt{3}kT}\right)} \quad (5)$$

In the current study, we assume that the concentration of flow defects c_f corresponds to the equilibrium state in the Newtonian flow region. In the Newtonian domain, $\sigma_f V$ is much smaller than kT , and the term $\sinh(\sigma_f V / 2\sqrt{3}kT)$ can be simplified as $\sigma_f V / 2\sqrt{3}kT$. Hence, the Newtonian viscosity η_N can be written as:

$$\eta_N = \frac{2\sqrt{3}kT}{3\dot{\varepsilon}_0 V} \quad (6)$$

The Newtonian viscosity η_N at a certain temperature can be determined, and the detail information is marked in the dash frame of Fig. 5, i.e. 9.81×10^{11} , 2.54×10^{11} , and 7.49×10^{10} Pa·s for $T = 643$, 653 , and 663 K, respectively.

The apparent activation energy during the deformation process, Q_{app} , can be described by the Arrhenius equation: $\eta_N = \eta_0 \exp(Q_{app}/kT)$, where η_0 is a viscosity constant, η_N is the Newtonian viscosity. The relationship between the Newtonian viscosity η_N and the reciprocal of test temperature of $Zr_{65}Cu_{18}Ni_7Al_{10}$ bulk metallic glass is shown in Fig. 8. Through the slope of the fitting curve, the apparent activation energy on high temperature compression process for the $Zr_{65}Cu_{18}Ni_7Al_{10}$ bulk metallic glass $Q_{app} = 4.73 \pm 0.10$ eV can be determined, which is in good agreement with that of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (4.6 eV) [12] and $Zr_{55}Al_{10}Ni_5Cu_{30}$ (5.1 eV) [34].

On the other hand, a master curve of the normalized viscosity η/η_N can be obtained at different temperatures by the stretched exponential function or Kohlrausch–Williams–Watts (KWW) model according to the previous theoretical

approach [15]:

$$\frac{\eta}{\eta_N} = 1 - \exp \left[- \left(\frac{\sigma_{tc}}{\dot{\varepsilon} \eta_N} \right)^{\beta_{KWW}} \right] \quad (7)$$

where σ_{tc} and β_{KWW} are the fitting parameters. σ_{tc} can be regarded as a transition point of characteristic stress and β_{KWW} is associate with the slope of the non-Newtonian viscosity. As shown in Fig. 9, the curve can be well fitted by Eq. (7). The transition characteristic stress $\sigma_{tc} = 118$ MPa corresponds to a transformation from Newtonian to non-Newtonian flow in the normalized viscosity curve. $\beta_{KWW} = 0.78$ falls near the range of other Zr-based metallic glass, $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ [15], $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ [35] and La-based metallic glass, $La_{60}Ni_{15}Al_{25}$ [24], which exhibits the degree of deviation from the Newtonian flow.

Another approach that can unify the variations of the viscosity with different strain rates and temperatures to a master curve is to combine Eqs. (5) and (6), hence η/η_N can be represented by [16]:

$$\frac{\eta}{\eta_N} = \frac{\sigma V / 2\sqrt{3}kT}{\sinh(\sigma V / 2\sqrt{3}kT)} = \frac{x}{\sinh(x)} \quad (8)$$

Fig. 10 displays the variation of η/η_N with $x = \sigma V / 2\sqrt{3}kT$, all the point calculated by the experimental data at different strain rates and temperatures stand with a good precision in the master curve of a function $x/\sinh x$ [16].

4.3 Strain rate sensitivity exponent

Fig. 11 illustrates the variation of the steady state flow stress with the strain rate for $Zr_{65}Cu_{18}Ni_7Al_{10}$ metallic glass at different temperatures. Strain rate sensitivity exponent, defined as $m = \partial \log \sigma_f / \partial \log \dot{\varepsilon}$ [36], can reflect the rheological regime. In the homogeneous deformation process, with higher testing temperature or smaller

strain rate, the strain rate sensitivity exponent is closer to unity, which also indicates that the state is closer to Newtonian fluid, as shown in Fig.11. Based on the previous experimental observations [15, 16], the Newtonian flow will emerge in a small strain rate at certain testing temperature.

It is essential to investigate the transition time from Newtonian to non-Newtonian flow at a certain temperature. The activation volume V and frequency factor $\dot{\varepsilon}_0$ can be obtained by using Eq. (3). Combining Eq. (3) and the fitting parameters (activation energy and frequency factor), the relation of steady state flow stress versus strain rate can be expanded, with greater strain rate ranges from 10^{-7} s^{-1} to 10^{-2} s^{-1} [14]. As shown in Fig. 12, although there exists a clear line segment at lower strain rate on each line, which is with respect to a Newtonian flow at lower strain rate, major questions remain to be answered about the transition strain rate from Newtonian to non-Newtonian [15].

From the definition of strain rate sensitivity exponent, the relationship between strain rate sensitivity exponent and the corresponding strain rate can be calculated based on the expended steady state flow stress - strain rate curve (Fig. 12). As illustrated in Fig. 13, there exists an obvious transition strain rate on each steady state flow stress-strain rate curve. The deviation from Newtonian flow has been observed in the SLR, however, the transport coefficients (such as the self-diffusion coefficient, viscosity, etc.) deviates from the Arrhenius behavior at higher temperature, where liquids behave more like solids in the glass formation process [37, 38]. The temperature is defined as Arrhenius crossover T_A , which is an essential parameter in the metallic glass analysis with a wider range of amorphous domain. Although the

temperature range is not consistent, a deviation from the straight line is observed in the glass formation process, and the low temperature glassy characteristics can be determined by the value of T_A in liquid [39, 40], which could be an important research issue with respect to glass-forming metallic liquid.

In this research, the transition strain rate are $2.3 \times 10^{-5} \text{ s}^{-1}$, $1 \times 10^{-4} \text{ s}^{-1}$, and $3.86 \times 10^{-4} \text{ s}^{-1}$ at the temperature of 643 K, 653K, and 663 K, respectively. The variation of transition strain rate $\dot{\epsilon}_{tr}$ with the corresponding temperature T can be described by the Arrhenius empiric equation. Fig. 14 shows the Arrhenius plot of the variation of transition strain rate $\dot{\epsilon}_{tr}$ versus the reciprocal of absolute temperature. Through the slope of the fitting curve, the apparent activation energy of transition from Newtonian flow to non-Newtonian flow for the $\text{Zr}_{65}\text{Cu}_{18}\text{Ni}_7\text{Al}_{10}$ bulk metallic glass can be determined ($Q_{tr} = 5.19 \pm 0.08 \text{ eV}$), which is similar to the apparent activation energy of frequency factor $\dot{\epsilon}_0$ in Eq. (4).

5. Conclusion

High temperature deformation of the $\text{Zr}_{65}\text{Cu}_{18}\text{Ni}_7\text{Al}_{10}$ bulk metallic glass has been investigated in the supercooled liquid region. The current research proves the existence of a transition from Newtonian to non-Newtonian flow in compression of bulk metallic glasses at high temperature. The physically significance of parameter σ_{tc} could be analyzed, , which represents the characteristic stress from Newtonian to non-Newtonian flow in the master curve and can be obtained by fitting the stretched exponential function. The relationship between strain rate sensitivity exponent and the corresponding strain rate is determined, and the variation of transition strain rate from Newtonian to non-Newtonian flow at different temperatures are obtained.

The four Arrhenius activation processes have been investigated in the supercooled region: (1) the stimulus frequency versus the dynamic glass transition temperature T_α ; (2) the frequency factor versus the corresponding temperature; (3) the normalized viscosity versus the corresponding temperature; (4) the transition strain rate from Newtonian to non-Newtonian flow versus the corresponding temperature. Energies in the four activation processes are all about 5 eV, which could be considered as four sides of the same physical event. The difference is mainly caused by different external stimulations.

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Figures

Fig. 1. The XRD pattern of the $\text{Zr}_{65}\text{Cu}_{18}\text{Ni}_7\text{Al}_{10}$ bulk metallic glass after experiment.

Fig. 2. A typical DSC curve at a heating rate of 20K/min.

Fig. 3. The temperature dependence of loss modulus for $\text{Zr}_{65}\text{Cu}_{18}\text{Ni}_7\text{Al}_{10}$ bulk metallic glass at a heating rate of 3 K/min for different frequencies. (Insert: an Arrhenius plot of peak frequency of loss modulus versus the reciprocal of temperature.)

Fig. 4. A typical true compressive stress-strain curve of the $\text{Zr}_{65}\text{Cu}_{18}\text{Ni}_7\text{Al}_{10}$ bulk metallic glass during strain rate jump tests from 1×10^{-4} to $2.5 \times 10^{-3} \text{ s}^{-1}$ at 643 K.

Fig. 5. The apparent viscosity η at various strain rates and temperatures. Newtonian viscosity η_N displayed in the left of figure.

Fig. 6. Variation of the flow stress with the applied strain rate in $\text{Zr}_{65}\text{Cu}_{18}\text{Ni}_7\text{Al}_{10}$ metallic glass at different temperatures (the lines are deduced from Eq. (3))

Fig. 7. An Arrhenius plot of frequency factor versus the reciprocal of temperature.

Fig. 8. An Arrhenius plot of Newtonian viscosity η_N versus the reciprocal of temperature.

Fig. 9. A master curve of the normalized viscosity η/η_N versus $\dot{\epsilon} \cdot \eta_N$ in $\text{Zr}_{65}\text{Cu}_{18}\text{Ni}_7\text{Al}_{10}$ bulk metallic glass at different temperatures.

Fig. 10. Deduced master curve for the normalized x , according to Eq. (8) (the line is a function curve of $x/\sinh x$).

Fig. 11. The variation of the steady state flow stress with strain rate in $\text{Zr}_{65}\text{Cu}_{18}\text{Ni}_7\text{Al}_{10}$ bulk metallic glass at different temperatures (strain rate sensitivity exponent m marked in adjacent strain rate).

Fig. 12. The variation of the steady state flow stress with strain rate in $\text{Zr}_{65}\text{Cu}_{18}\text{Ni}_7\text{Al}_{10}$ bulk metallic glass at different temperatures with strain rate range from 10^{-7} s^{-1} to 10^{-2} s^{-1} .

Fig. 13. The strain rate dependence of strain rate sensitivity exponent at different temperatures.

Fig. 14. An Arrhenius plot of transition strain rate $\dot{\epsilon}_{tr}$ versus the reciprocal of temperature.

Tables

Table I Activation volume V and frequency factor $\dot{\varepsilon}_0$ obtained from fitting the experimental data in $\text{Zr}_{65}\text{Cu}_{18}\text{Ni}_7\text{Al}_{10}$ bulk metallic glass.

Temperature (K)	Frequency factor $\dot{\varepsilon}_0$ (s^{-1})	Activation volume V (nm^3)
643	4.58×10^{-5}	0.24618
653	2.01×10^{-4}	0.21922
663	8.07×10^{-4}	0.18842

Table II Activation volume V in the typical Zr-based bulk metallic glasses obtained from the experimental results (As-cast samples).

BMGs	Activation volume(nm^3)	Reference
$\text{Cu}_{40}\text{Zr}_{44}\text{Ag}_8\text{Al}_8$	0.236–0.372	[25]
$\text{Cu}_{36}\text{Zr}_{48}\text{Al}_8\text{Ag}_8$	0.19–0.23	[26]
$\text{Zr}_{52.5}\text{Al}_{10}\text{Cu}_{27}\text{Ti}_{2.5}\text{Ni}_8$	0.156–0.242	[27]
$\text{Zr}_{52.5}\text{Al}_{10}\text{Cu}_{22}\text{Ti}_{2.5}\text{Ni}_{13}$	0.149–0.201	[27]
$\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$	0.20–0.23	[28]
$\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$	0.215–0.230	[29]
$\text{Zr}_{65}\text{Cu}_{18}\text{Ni}_7\text{Al}_{10}$	0.188-0.246	Current work