Effects of Nb microalloying on properties of Zr-Al-Fe-Cu glassy alloy

De-chuan Yu, Chong-wei Zheng, Qiong Qin, Chun-xin Li, Xue-hong Li, Di Wu, Yang Qi, Hai-feng Zhang, Yong Wang and Yue Yu

Original content from this work may be used under the terms of the Creative Commons Attribution 4.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

Abstract
The effects of Nb-microalloying on glass forming ability, thermal properties and mechanical properties of \((\text{Zr}_{0.6032}\text{Cu}_{0.2256}\text{Fe}_{0.0995}\text{Al}_{0.0717})_{1-x}\text{Nb}_x (x = 0, 1, 2, 3, 4)\) alloys were investigated. The best glass former was obtained for \((\text{Zr}_{0.6032}\text{Cu}_{0.2256}\text{Fe}_{0.0995}\text{Al}_{0.0717})_{0.97}\text{Nb}_{0.03}\), which could be fabricated into full glass with diameter up to 6 mm at least. In addition, the origin of enhancing GFA of ZrAlFeCu amorphous alloy by means of the minor addition of Nb, Gd and Hf, was also discussed from the aspects of clusters and mixing entropy, which might provide a method of understanding the mechanism of enhancing glass-forming ability via microalloying, and choosing minor alloying element with an aim of enhancing glass-forming ability. It was found that the thermal stability reduced as the content of Nb increased along with the supercooled liquid region decreased. Nb-microalloying decreased the fracture strength. However, moderate Nb microalloying could enhance the room temperature plastic strain.

1. Introduction
Owing to the high glass-forming ability (GFA), good biocompatibility, excellent mechanical properties and high corrosion resistance, Zr-based bulk metallic glasses (BMGs) have been chosen as a candidate for biomedical applications [1–3]. In recent years, a series Be-free Zr-based BMGs have been developed, such as in Zr-Al-Fe, Zr-Al-Fe-Cu, Zr-Al-Ni, Zr-Al-Cu and Zr-Al-Co-Ag etc systems [4–8]. Among the designed Zr-based glass formers, those containing Ni element are blamed for being allergic and possibly carcinogenic [7]. Besides, considering the cost of manufacturing, glass-formers containing noble metal, might hinder the application. Based on this, taking into account various factors such as manufacturability, the cost and the mechanical properties, Zr-Al-Fe-Cu BMGs are attractive, and the experimental results have shown the feasibility of biomedical devices applications reported by Jin and Han et al researchers [2, 9].

GFA is one of paramount factors influencing manufacturability and application range. Minor element alloying is an effective way to improve glass forming ability [10, 11]. Among the microalloying elements, Nb plays an important role in enhancing GFA of Fe-based, Ni-based, Co-based, Ce-based, La-based, Gd-based and Zr-based etc various amorphous alloys [3, 11–18]. In our previous work, a method combining clusters and mixing entropy was applied to understand glass formation and design good glass formers [19]. Under the guidance of this method, a novel Ni-free Zr-based glass former \(\text{Zr}_{0.32}\text{Cu}_{0.22}\text{Fe}_{0.95}\text{Al}_{0.17}\) was designed with a critical diameter up to 5 mm, superior to the well-known composition \(\text{Zr}_{61}\text{Cu}_{25}\text{Fe}_{5}\text{Al}_{10}\) BMG under the same laboratory condition, which shows a good prospect for future application as biomedical materials [20].
As mentioned above, Nb-microalloying always plays an important role in enhancing GFA and changing properties. However, the discussion on the mechanism of Nb-microalloying understood via microstructure is quite few. Based on this, the effects of minor addition of Nb on GFA, thermal properties and mechanical properties of Zr60.32Cu22.56Fe9.95Al7.17 have been investigated. The reasons for influencing GFA, thermal properties and mechanical properties were discussed from the aspect of clusters and mixing entropy with an aim of offering a method of understanding the mechanism of microalloying, which might lay a solid foundation of helping us quickly and exactly choose the beneficial microalloying elements.

2. Materials and methods

Zr-based alloys with compositions of \((\text{Zr}_{0.6032}\text{Cu}_{0.2256}\text{Fe}_{0.0995}\text{Al}_{0.0717})_{100-x}\text{Nb}_x (x = 0, 1, 2, 3, 4)\) and \((\text{Zr}_{0.6032}\text{Cu}_{0.2256}\text{Fe}_{0.0995}\text{Al}_{0.0717})_9\text{Gd}_1\) were prepared in a Ti-gettered argon atmosphere. To ensure the homogeneity, the master alloys were melted four times. The purities of elements are 99.99 wt. % for Al, Fe, Cu, 99.95 wt. % for Zr and Gd. Bulk samples with diameters of 2 mm and 6 mm were produced by copper mold suction casting. The ribbons \((0.02 \text{ mm} \times 1.2 \text{ mm})\) were fabricated by melt spinning. The structure of the sample was identified by x-ray diffraction (XRD, Philips PW 1050, Cu K\(\alpha\)). The thermodynamic parameters of glassy rods, such as the glass transition temperatures and the liquids temperatures etc, were evaluated using differential scanning calorimetry (DSC, Netzsch DSC 404C) at a heating rate of 0.67 K s\(^{-1}\). The compression properties were tested, using samples having 4 mm long and 2 mm diameter, by Instron testing machine at a strain rate of \(5.0 \times 10^{-4} \text{ s}^{-1}\). The fracture features of the specimens were observed by scanning electron microscope (SEM, Supra 35).

3. Results and discussion

Figure 1 shows the XRD patterns of the casted \((\text{Zr}_{0.6032}\text{Cu}_{0.2256}\text{Fe}_{0.0995}\text{Al}_{0.0717})_{100-x}\text{Nb}_x (x = 0, 1, 2, 3, 4)\) alloys with diameters of 6 mm. Under the same laboratory environment, the XRD pattern of Zr60.32Cu22.56Fe9.95Al7.17 \((x = 0)\) with a diameter of 5 mm was examined and shown in our previous paper [20]. The results showed that \(\text{Zr}_{60.32}\text{Cu}_{22.56}\text{Fe}_{9.95}\text{Al}_{7.17}\) s could form full amorphous alloy with diameter up to 5 mm. However, as shown in figure 1, the XRD pattern of \(\text{Zr}_{60.32}\text{Cu}_{22.56}\text{Fe}_{9.95}\text{Al}_{7.17}\) exhibits apparent crystalline Bragg peaks indicating that its critical diameter is 5 mm. The XRD patterns of the as-cast \((\text{Zr}_{0.6032}\text{Cu}_{0.2256}\text{Fe}_{0.0995}\text{Al}_{0.0717})_9\text{Nb}_1\) and \((\text{Zr}_{0.6032}\text{Cu}_{0.2256}\text{Fe}_{0.0995}\text{Al}_{0.0717})_9\text{Gd}_1\) rods with critical diameters of 6 mm consist of apparent crystalline Bragg peaks. It can be inferred that \(\text{Zr}_{60.32}\text{Cu}_{0.2256}\text{Fe}_{0.0995}\text{Al}_{0.0717}\) \((x = 3)\) couldn’t form full glassy rods with diameters of 6 mm. When \(x = 4\), the glass forming ability is apparently improved as the crystalline Bragg peaks are apparently restrained. \((\text{Zr}_{0.6032}\text{Cu}_{0.2256}\text{Fe}_{0.0995}\text{Al}_{0.0717})_9\text{Nb}_1\) could form full glass with diameter up to 6 mm. However, with higher Nb content alloying \((x = 4)\), sample with a
diameter up to 6 mm exhibits crystalline Bragg peaks indicating that \(Zr_{60.32}Cu_{0.2256}Fe_{0.0995}Al_{0.0717}\) alloy possesses the highest GFA in this series.

As can be concluded above, the critical diameter of \(Zr_{60.32}Cu_{0.2256}Fe_{0.0995}Al_{0.0717}\) increased from 5 mm to 6 mm with the addition of 3at% Nb. As one of effective ways of enhancing glass forming ability, the internal mechanism of minor alloying is still unclear from the aspect of clusters. It is essential to figure out the origin of high GFA of \(Zr_{60.32}Cu_{0.2256}Fe_{0.0995}Al_{0.0717}\) before understanding the mechanism of enhancing GFA via microalloying.

In our previous work, a method combining clusters and mixing entropy was applied to understand glass formation and design good glass formers [19]. Essentially, this method of understanding glass forming ability balances both microstructure and thermodynamics. Under the guidance of this method, clusters were treated as the basic units of glass formers. The coefficients of clusters are calculated based on the premise that composition owns the corresponding largest mixing entropy.

Under the guidance of this method, glass formation in Zr-Al-Fe-Cu system was studied in our previous work [20]. The best glass former \(Zr_{60.32}Cu_{0.2256}Fe_{0.0995}Al_{0.0717}\) could be expressed as

\[
\begin{align*}
  \text{Fe} & (Zr_{0.6} + Zr_{0.4}) + 0.961 \text{Al}(Zr_{0.6} + Al_{0.4}) + 1.511 \text{Cu}(Cu_{0.5} + Zr_{0.5}), \\
  \text{Al}(Zr_{0.6} + Al_{0.4}) + \text{Cu}(Cu_{0.5} + Zr_{0.5})
\end{align*}
\]

These Zr-Fe, Zr-Al and Zr-Cu topological clusters are the basic units of this glass former. The high topological packing in clusters and high entropy are the origin of high GFA of \(Zr_{60.32}Cu_{0.2256}Fe_{0.0995}Al_{0.0717}\).

The enthalpies of mixing of the atomic pairs Nb-Zr, Nb-Al, Nb-Fe and Nb-Cu at equi-atomic compositions are respectively \(\Delta H_{\text{Nb-Zr}} = 4 \text{KJ mol}^{-1}\), \(\Delta H_{\text{Nb-Al}} = -18 \text{KJ mol}^{-1}\), \(\Delta H_{\text{Nb-Fe}} = -16 \text{KJ mol}^{-1}\) and \(\Delta H_{\text{Nb-Cu}} = -5 \text{KJ mol}^{-1}\) [21]. The negative enthalpies of mixing mean the tendentiousness of gathering together to form clusters. However, it has been pointed that, to enhance GFA of basic composition, the microalloying element enjoying negative enthalpies of mixing between component elements is a prerequisite but not sufficient condition. The key to enhancing GFA is introducing topological clusters.

As analyzed above, Nb-Fe and Nb-Al pairs are negative. They are likely to gather together to form clusters. Miracle pointed that, the cluster was similar to the microstructure of competing phases. As for Nb-Al binary pairs, it has been reported that Nb and Al could form topologically packed Al-centered Al-Al, Nb-Al, and Cu-Al clusters. These topologically packed clusters could increase the degree of atomic packing state, which is beneficial for glass-formation. Moreover, Nb is adjacent to Zr in the periodic table of the elements. Nb element might take the place of the position of Zr in Zr-based clusters, namely changing from Zr-Al, Zr-Fe binary clusters to Zr/Nb-Al and Zr/Nb-Fe clusters, which might enhance the degree of clusters’ topological packing.

For the Zr-based amorphous alloys, except Nb element, rare-earth element was also one of the important microalloying elements [24]. To further study the mechanism of rare-earth element microalloying, similarly, 3 at% Gd was also microalloying to \(Zr_{60.32}Cu_{0.2256}Fe_{0.0995}Al_{0.0717}\). As shown in figure 1, the GFA of \(Zr_{60.32}Cu_{0.2256}Fe_{0.0995}Al_{0.0717}\) increased from 5 mm to at least 6 mm.

---

**Figure 2.** Images of clusters (a: Cluster Fe-Nb, b: Cluster Fe-Cu, c: Cluster Al-Al-Gd derived from phase Al$_2$Gd).
The enthalpies of mixing of the atomic pairs Gd-Zr, Gd-Al, Gd-Fe and Gd-Cu at equi-atomic compositions are respectively \( \Delta H_{\text{Gd-Zr}} = 9 \text{ KJ mol}^{-1} \), \( \Delta H_{\text{Gd-Al}} = -39 \text{ KJ mol}^{-1} \), \( \Delta H_{\text{Gd-Fe}} = -1 \text{ KJ mol}^{-1} \) and \( \Delta H_{\text{Gd-Cu}} = -22 \text{ KJ mol}^{-1} \) [21]. In our previous study, a CN12 cluster Al-Al\(_6\)Gd\(_6\) was obtained from Al\(_2\)Gd [19]. Similarly, as shown in figure 2, a CN12 cluster Fe-Fe\(_6\)Gd\(_6\) could be obtained from phase Fe\(_2\)Gd. The Goldschmidt radiuses of Gd, Fe and Al are 0.180 nm, 0.128 nm and 0.143 nm, separately. Similar to the calculation of Nb-Fe cluster, the actual radius ratios of Fe-Fe\(_6\)Gd\(_6\) and Al-Al\(_6\)Gd\(_6\) are 0.831 and 0.885. The deviation of calculation results and theoretical value are \(-7.87\%\) and \(-1.89\%\). The above two Fe-Fe\(_6\)Gd\(_6\) and Al-Al\(_6\)Gd\(_6\) can be treated as topologically packed clusters. The new topologically packed clusters introduced by Gd-microalloying, could increase the degree of atomic packing state, thus enhancing the GFA of basic composition.

Similarly, it has been proven effective in enhancing GFA of ZrAlFeCu amorphous alloys via Hf-microalloying [2]. It could also be explained via clusters. The enthalpies of mixing of the atomic pairs Hf-Zr, Hf-Al, Hf-Fe and Hf-Cu at equi-atomic compositions are respectively \( \Delta H_{\text{Hf-Zr}} = 0 \text{ KJ mol}^{-1} \), \( \Delta H_{\text{Hf-Al}} = -39 \text{ KJ mol}^{-1} \), \( \Delta H_{\text{Hf-Fe}} = -21 \text{ KJ mol}^{-1} \) and \( \Delta H_{\text{Hf-Cu}} = -17 \text{ KJ mol}^{-1} \) [21]. The enthalpies of mixing of Hf-Al, Hf-Fe and Hf-Cu binary pairs are negative, which means the tendency of gather together to form clusters. As shown in figure 3, an Archimedean octahedral anti-prism CN10 cluster Al–Al\(_2\)Hf\(_8\) is obtained from phase AlHf\(_2\). Two CN12 clusters Fe-Fe\(_6\)Hf\(_6\) and Fe-Fe\(_3\)Hf\(_9\) are obtained from phase Fe\(_2\)Hf and FeHf\(_2\). The Goldschmidt radiuses of Hf, Fe and Al are 0.159 nm, 0.128 nm and 0.143 nm, separately. The ideal radius ratios of CN10 and CN12 cluster are 0.799 and 0.902 [23]. As for Al–Al\(_2\)Hf\(_8\), Fe-Fe\(_6\)Hf\(_6\) and Fe-Fe\(_3\)Hf\(_9\) clusters, the actual radius ratios are 0.918, 0.892 and 0.846. The deviation of calculation results and theoretical value are \(-1.11\%\) and \(-6.21\%\). It can be seen that, Fe-Fe\(_6\)Hf\(_6\) and Fe-Fe\(_3\)Hf\(_9\) clusters are topologically packed clusters. As for Hf-Cu binary system, a series of topologically packed clusters Cu–Cu\(_2\)Hf\(_4\), Cu–Cu\(_3\)Hf\(_4\) and Cu–Cu\(_5\)Hf\(_5\) have been found and used to design good glass-formers in Cu-Hf-Al system [25]. Moreover, Hf and Zr are in the same group on the periodic table. They share similar atomic radius, physical properties and chemical properties. Hf might take the place of the position of Zr in Zr-based clusters, namely changing from Zr-Al, Zr-Fe and Zr-Cu binary clusters to Zr/Hf-Al, Zr/Hf-Fe and Zr/Hf-Cu clusters, which might enhance the degree of topological packing.

Figure 3. Images of clusters (a: Cluster Al-Al\(_2\)Hf\(_8\) derived from phase AlHf\(_2\), b: Cluster Fe-Fe\(_6\)Hf\(_6\) derived from phase Fe\(_2\)Hf, c: Cluster Fe-Fe\(_3\)Hf\(_9\) derived from phase FeHf\(_2\)).

Figure 4. DSC curves of as-cast (Zr\(_{0.6032}\)Cu\(_{0.2256}\)Fe\(_{0.0995}\)Al\(_{0.0717}\))\(_{100-x}\)Nb\(_x\) (x = 0, 1, 2, 3, 4) metallic glass alloy series, showing their (a) crystallization and (b) melting behaviors.
It can be seen that, Nb-, Gd- and Hf-microalloying could enhance the GFA of ZrAlFeCu amorphous alloys. On one hand, from the point of clusters, with the addition of Nb/Gd/Hf element, the newly introduced topologically clusters might enhance the degree of atomic packing state, which is beneficial for glass formation. On the other hand, from the point of entropy, with the addition of Nb/Gd/Hf, the degree of chaos of the system rising, it would be more difficult for the precipitation of crystalline phases which is also beneficial for glass formation.

It can be inferred that, due to the topologically packed Al-Al₈Nb₄, Fe-Nb₇.₅Fe₄.₅, Fe-Fe₆Gd₆, Al-Al₆Gd₆, Fe-Fe₃Hf₉, Fe-Fe₆Hf₆ clusters, Nb-, Gd- and Hf-microalloying might be effective in enhancing the GFA of the amorphous alloys containing with element Al or Fe. Furthermore, these Hf-based and Gd-based binary topologically packed clusters could help researchers further develop Hf-based and Gd-based glass-formers.

Table 1. Thermal parameters of (Zr₆₀.₆₃Cu₂₂.₃₆Fe₀.₉₉₅Al₀.₇₁₇)₁₀₀₋ₓNx (x = 0, 1, 2, 3, 4) metallic glass alloy series.

| Alloys           | Tg (K) | Tx (K) | Tm (K) | Tl (K) |
|------------------|--------|--------|--------|--------|
| Zr₆₀.₆₃Cu₂₂.₃₆Fe₀.₉₉₅Al₀.₇₁₇ | 663.8  | 742.9  | 1126.7 | 1231.6 |
| (Zr₆₀.₆₃Cu₉₂.₂₄Fe₀.₀₉₉₅Al₀.₇₁₇)ₙₓNb₁ | 666.₉  | 7₃₉.₄  | 110₈.₉ | 12₂₈.₄ |
| (Zr₆₀.₆₃Cu₂₂.₃₆Fe₀.₀₉₉₅Al₀.₇₁₇)ₙₓNb₂ | 6₆₉.₇  | 7₃₄.₆  | 110₅.₉ | 1₂₁₉.₆ |
| (Zr₆₀.₆₃Cu₂₂.₃₆Fe₀.₀₉₉₅Al₀.₇₁₇)ₙₓNb₃ | 6₇₁.₆  | 7₃₂.₉  | 1₁₀₄.₂ | 1₂₁₀.₄ |
| (Zr₆₀.₆₃Cu₂₂.₃₆Fe₀.₀₉₉₅Al₀.₇₁₇)ₙₓNb₄ | 6₇₆.₂  | 7₃₃.₈  | 1₁₀₇.₃ | 1₂₀₇.₈ |

Table 2. Thermal parameters of (Zr₆₀.₆₃Cu₂₂.₃₆Fe₀.₉₉₅Al₀.₇₁₇)₁₀₀₋ₓNx (x = 0, 1, 2, 3, 4) metallic glass alloy series.

| Alloys           | ΔT (K) | Tg (K) | γ | γₘ |
|------------------|--------|--------|---|----|
| Zr₆₀.₆₃Cu₂₂.₃₆Fe₀.₉₉₅Al₀.₇₁₇ | 7₉₆.₁  | 0.₅₃₉ | 0.₃₉₂ | 0.₆₆₇ |
| (Zr₆₀.₆₃Cu₂₂.₃₆Fe₀.₉₉₅Al₀.₇₁₇)ₙₓNb₁ | 7₂₅.₅  | 0.₅₄₃ | 0.₃₉₀ | 0.₆₆₁ |
| (Zr₆₀.₆₃Cu₂₂.₃₆Fe₀.₉₉₅Al₀.₇₁₇)ₙₓNb₂ | 6₄₉.₄  | 0.₅₄₉ | 0.₄₁₄ | 0.₆₅₆ |
| (Zr₆₀.₆₃Cu₂₂.₃₆Fe₀.₉₉₅Al₀.₇₁₇)ₙₓNb₃ | ₆₁₃.₅  | 0.₅₅₅ | 0.₃₈₉ | 0.₆₅₆ |
| (Zr₆₀.₆₃Cu₂₂.₃₆Fe₀.₉₉₅Al₀.₇₁₇)ₙₓNb₄ | ₅₇₆.₂  | 0.₅₆₀ | 0.₃₈₉ | 0.₆₅₅ |

Figure 5. Relationship between the Tx, Tg, ΔT, Tm and Tl values and content of Nb for (Zr₆₀.₆₃Cu₂₂.₃₆Fe₀.₉₉₅Al₀.₇₁₇)₁₀₀₋ₓNx (x = 0, 1, 2, 3, 4) metallic glasses.
the glass transition temperature ($T_g$) of this system increases along with the content of Nb increases. When the content of Nb does not exceed 3 at%, the crystallization temperature ($T_x$) of this system increases along with the content of Nb increases, while the content of Nb increases to 4 at.%, the crystallization temperature slightly decreased.

Figure 4(b) shows the melting behaviors of ($Zr_{60.32}Cu_{22.56}Fe_{9.95}Al_{7.17}$)$_{100-x}$Nb$_x$ ($x = 0, 1, 2, 3, 4$) metallic glass alloys. It can be seen that minor addition of Nb doesn’t change the melting process of $Zr_{60.32}Cu_{22.56}Fe_{9.95}Al_{7.17}$. All of the curves show a distinct endothermic peak and a weak endothermic peak, indicating these alloys have multiple melting phases.

It can be seen that, with the addition of Nb, the supercooled liquid region $\Delta T$ decreases, along with the thermal stability getting worse. However, moderate minor Nb addition could enhance the glass forming ability. It can be inferred that, in the system of Zr-Al-Cu-Nb, the width of the supercooled liquid region $\Delta T$ could not properly describe the glass forming ability. As stated above, a series of thermal parameters $T_{fg}$, $\gamma_T$, and $\gamma_m$ have been proposed to predict the glass forming ability. However, combining table 2 and figure 1, all of the parameters couldn’t represent the glass-formation ability well.

As can be seen in figure 5 and table 2, with the addition of Nb, the supercooled liquid region $\Delta T$ decreases, along with the thermal stability get worse. As analyzed above, the enthalpies of mixing of the atomic pairs Nb-Zr and Nb-Cu are positive quite close to zero, Nb has an aggregation phenomenon. With excessive Nb element doping, the phenomenon of aggregation is enhanced, which would promote the formation of Nb-rich clusters, increase the possibility of nucleation and precipitation, decrease the thermal stability of alloys in supercooled liquid region, thus causes narrowing of the width of supercooled liquid region in DSC curves.

The number of short-range order clusters and activation energy have a close relationship [29]. Based on the DSC curves of ($Zr_{60.32}Cu_{0.2256}Fe_{0.0995}Al_{0.0717}$)$_{100-x}$Nb$_x$ ($x = 0, 1, 2, 3, 4$) amorphous ribbons at the heating rates of 0.167 K s$^{-1}$, 0.333 K s$^{-1}$, 0.5 K s$^{-1}$, 0.667 K s$^{-1}$ and 0.833 K s$^{-1}$, under the guidance of Kissinger equation [30], the corresponding Kissinger plots of ($Zr_{60.32}Cu_{0.2256}Fe_{0.0995}Al_{0.0717}$)$_{100-x}$Nb$_x$ ($x = 0, 1, 2, 3, 4$) are shown in figure 6. The activation energies for crystallization growth $E_p$ of ($Zr_{60.32}Cu_{0.2256}Fe_{0.0995}Al_{0.0717}$)$_{100-x}$Nb$_x$ ($x = 0$, 1, 2, 3, 4) have been obtained. For $x = 0, 1, 2, 3$ and 4, the $E_p$ are separately 190.5 kJ mol$^{-1}$, 218.9 kJ mol$^{-1}$, 218.0 kJ mol$^{-1}$, 222.2 kJ mol$^{-1}$ and 282.6 kJ mol$^{-1}$. Compared to primary composition $Zr_{60.32}Cu_{32.56}Fe_{9.95}Al_{17.1}$ with Nb-microalloying, the activation energies for crystallization growth $E_p$ for ($Zr_{60.6032}Cu_{0.2256}Fe_{0.0995}Al_{0.0717}$)$_{100-x}$Nb$_x$ ($x = 0, 1, 2, 3, 4$) increased. $E_p$ stands for the activation energy of the growth of crystalline phases. One of the steps of growth of crystal phases is breaking down the local structure (cluster) to form ordered crystalline phases. However, the clusters in this paper obtained according to the Miracle theory, enjoy special asymmetry and high degree of topological packing. Firstly, from the point of thermal dynamics, the high topologically packed clusters would increase viscosity of molten alloy, which would increase the difficulty of the growth of crystalline phases. Secondly, from the point of energy, the high topologically packed clusters would also decrease the thermodynamic free volume, thus decreasing the energy of system, leading a more stable state, which would also increase the difficulty of the growth of crystalline phases [25]. Thirdly, from the shape of clusters, forming ordered crystalline phases need break down more clusters due to the special asymmetry of obtained clusters, which would also enhance the difficulty of crystalline phases.
**Figure 7.** Nominal compressive stress-strain curves for the $(Zr_{0.6032}Cu_{0.2256}Fe_{0.0995}Al_{0.0717})_{100-x}Nb_x$ ($x = 0, 1, 2, 3, 4$) alloys.

**Table 3.** The mechanical parameters of as-cast $(Zr_{0.6032}Cu_{0.2256}Fe_{0.0995}Al_{0.0717})_{100-x}Nb_x$ ($x = 0, 1, 2, 3, 4$) glassy alloy series with a diameter of 2 mm under uniaxial compressive loading.

| Alloys                             | $\sigma_y$ (MPa) | $\sigma_m$ (MPa) | $\varepsilon_f$ (%) |
|-----------------------------------|------------------|------------------|---------------------|
| $Zr_{0.6032}Cu_{0.2256}Fe_{0.0995}Al_{0.0717}$ | 1583             | 1814             | 7.1                 |
| $(Zr_{0.6032}Cu_{0.2256}Fe_{0.0995}Al_{0.0717})_{99}Nb_1$ | 1585             | 1646             | 7.0                 |
| $(Zr_{0.6032}Cu_{0.2256}Fe_{0.0995}Al_{0.0717})_{98}Nb_2$ | 1467             | 1638             | 8.5                 |
| $(Zr_{0.6032}Cu_{0.2256}Fe_{0.0995}Al_{0.0717})_{97}Nb_3$ | 1593             | 1688             | 5.8                 |
| $(Zr_{0.6032}Cu_{0.2256}Fe_{0.0995}Al_{0.0717})_{96}Nb_4$ | 1627             | 1627             | 0                   |

**Figure 8.** SEM micrographs of surface morphology and fracture feature of as-cast $Zr_{0.6032}Cu_{0.2256}Fe_{0.0995}Al_{0.0717}$ glassy rod with a diameter of 2 mm after compression test under room temperature.
Growing Nb microalloying might bring more topologically packed clusters. As analyzed above, these clusters would greatly enhance the difficulty of the growth of crystal phases. Therefore, the activation energy of the growth of crystal phases $E_p$ would increase along with Nb doping.

As shown in figure 7, during the compression process, $(Zr_{0.6032}Cu_{0.2256}Fe_{0.0995}Al_{0.0717})_{100-x}Nb_x$ $(x = 0, 1, 2, 3)$ alloys have elastic strain and plastic strain. However, with 4 at. % Nb addition, the compressive deformation behavior displays a ductile-to-brittle transition. The compressive deformation behavior is sensitive to compositions.

The mechanical parameters of as-cast $(Zr_{0.6032}Cu_{0.2256}Fe_{0.0995}Al_{0.0717})_{100-x}Nb_x$ $(x = 0, 1, 2, 3, 4)$ glassy alloy series are shown in table 3. $\sigma_y$, $\sigma_m$ and $\varepsilon_f$ represent yield stress, maximum compressive strength and fracture strain, respectively. As can be seen in table 3, moderate Nb-microalloying could enhance the fracture strain.

Figures 8 and 9 shows the fracture features of the specimens of $Zr_{60.32}Cu_{22.55}Fe_{9.95}Al_{7.17}$ and $(Zr_{0.6032}Cu_{0.2256}Fe_{0.0995}Al_{0.0717})_{98}Nb_2$. As shown in figure 8(a), figures 9(a) and (c) the samples of $Zr_{60.32}Cu_{22.55}Fe_{9.95}Al_{7.17}$ and $(Zr_{0.6032}Cu_{0.2256}Fe_{0.0995}Al_{0.0717})_{98}Nb_2$ have typical vein-like and dimple patterns. It can be seen that, during the compression process, there forms a considerable amount of shear bands, which echoes the serrated rheological characteristics of room temperature compression curves of $Zr_{60.32}Cu_{22.55}Fe_{9.95}Al_{7.17}$ and $(Zr_{0.6032}Cu_{0.2256}Fe_{0.0995}Al_{0.0717})_{98}Nb_2$. As shown in figure 7, $(Zr_{0.6032}Cu_{0.2256}Fe_{0.0995}Al_{0.0717})_{98}Nb_2$.

As can be seen in figure 8(c), for the primary alloy composition $Zr_{60.32}Cu_{22.55}Fe_{9.95}Al_{7.17}$, there exists a small number of parallel and crossed shear bands. These shear bands are mostly in one direction. A certain amount of shear bands corresponds to the high plasticity. However, based on this, with 2 at% Nb further doping, the amount of shear bands increases significantly. The shear bands of $(Zr_{0.6032}Cu_{0.2256}Fe_{0.0995}Al_{0.0717})_{98}Nb_2$ have different directions. As can be in figure 9(b), interaction, restraint and divarication take place among the shear bands in different directions. Compared to the primary alloy composition $Zr_{60.32}Cu_{22.55}Fe_{9.95}Al_{7.17}$, the shear bands of $(Zr_{0.6032}Cu_{0.2256}Fe_{0.0995}Al_{0.0717})_{98}Nb_2$ are denser. These crossed, biforked and more dense shear bands in different directions correspond to the increase of compassion plasticity. Conversely, with 4 at% Nb further doping, there exist no shear bands of $(Zr_{0.6032}Cu_{0.2256}Fe_{0.0995}Al_{0.0717})_{98}Nb_4$. It can be more easily seen that the shear bands are closely relevant to plasticity.
As analyzed above, moderate Nb-microalloying would introduce new topologically packed clusters, which might be one of the important factors of influencing the initiation and propagation of shear bands. Conversely, the excessive Nb addition might change the microstructure of the system thereby hindering the generation of shear transformation and changing the compressive deformation behavior. The fracture morphology of \( (\text{Zr}_{0.6032}\text{Cu}_{0.2256}\text{Fe}_{0.0995}\text{Al}_{0.0717})_{100-x}\text{Nb}_x (x = 0, 1, 2, 3, 4) \) alloys is consistent with the results of compressive test.

### 4. Conclusions

The effects of Nb-microalloying on glass forming ability, thermal properties and mechanical properties of \( (\text{Zr}_{0.6032}\text{Cu}_{0.2256}\text{Fe}_{0.0995}\text{Al}_{0.0717})_{100-x}\text{Nb}_x (x = 0, 1, 2, 3, 4) \) alloys were investigated. The following conclusions can be reached from this study: moderate minor Nb addition could enhance the glass forming ability of Zr-Al-Fe-Cu system, and the best glass former was obtained for \( (\text{Zr}_{0.6032}\text{Cu}_{0.2256}\text{Fe}_{0.0995}\text{Al}_{0.0717})_{96}\text{Nb}_4 \), which could be fabricated into full glass with diameter up to 6 mm at least. The enhancement of GFA via Nb, Gd and Hf-microalloying of ZrAlFeCu amorphous alloy, could be contributed to the newly introduced topologically packed clusters and higher mixing entropy. A series of Hf-based and Gd-based binary topologically packed clusters have been found, which could help researchers further develop Hf-based and Gd-based glass-formers. The thermal stability reduced as the content of Nb increased along with the supercooled liquid region decreased. Nb-microalloying decease the fracture strength. Moderate Nb (2 at%) microalloying could enhance the room temperature plastic strain.

### Acknowledgments

This work was supported by the open fund project of State Key Laboratory of Numerical Modeling for Atmospheric Sciences and Geophysical Fluid Dynamics (LASG), Institute of Atmospheric Physics, the Chinese Academy of Sciences, and open fund project of Shandong Provincial Key Laboratory of Ocean Engineering, Ocean University of China (No. kloe201901).

### Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

### ORCID iDs

De-chuan Yu @ https://orcid.org/0000-0003-3861-1299  
Yang Qi @ https://orcid.org/0000-0001-6783-4171

### References

[1] Han K M, Qiang J B, Wang Y M and Haussler P 2017 Zr-Al-Co-Cu bulk metallic glasses for biomedical devices applications J. Alloy. Compd. 729 144–9  
[2] Han K M, Wang Y M, Qiang J B, Jiang H and Gu L W 2019 Low-cost Zr-based bulk metallic glasses for biomedical devices applications J. Non-Cryst. Solids 520 8  
[3] Yu D C, Li X, Wu X Y and Li S L 2019 Understanding and designing good glass formers in Zr-Al-Co-(Nb) system combining clusters and mixing entropy Mater. Lett. 234 291–3  
[4] Zhang Q S, Zhang W and Inoue A 2009 Ni-free Zr-Fe-Al-Cu bulk metallic glasses with high glass-forming ability Scr. Mater. 61 241–4  
[5] Li Y H, Zhang W, Dong C, Qiang J B, Xie G Q, Fujita K and Inoue A 2012 Glass-forming ability and corrosion resistance of Zr-based Zr-Ni-Al bulk metallic glasses J. Alloy. Compd. 536 S117–21  
[6] Inoue A and Takeuchi A 2011 Recent development and application products of bulk glassy alloys Acta Mater. 59 2243–67  
[7] Hua N B, Pang S J, Li Y, Wang J F, Li R, Georgarakis K, Yavari A R, Vaughan G and Zhang T 2011 Ni- and Cu-free Zr-Al-Co-Ag bulk metallic glasses with superior glass-forming ability J. Mater. Res. 26 539–46  
[8] Hua N B, Li R, Wang J F and Zhang T 2012 Biocompatible Zr-Al-Fe bulk metallic glasses with large plasticity Sci. China-Phys. Mech. Astron. 55 1664–9  
[9] Jin K and Loffler J F 2005 Bulk metallic glass formation in Zr-Cu-Fe-Al alloys Appl. Phys. Lett. 86  
[10] Lu Z P and Liu C T 2004 Role of minor alloying additions in formation of bulk metallic glasses: A Review J. Mater. Sci. 39 3965–74  
[11] Wang W H 2007 Roles of minor additions in formation and properties of bulk metallic glasses Prog. Mater. Sci. 52 540–96  
[12] Zhai F Q, Pineda E and Crespo D 2014 Role of Nb in glass formation of Fe-Mo-Co-M-B-Nb BMGs J. Alloy. Compd. 604 157–63  
[13] Wang Q, Zhu C L, Li Y H, Cheng X, Chen W R, Wu J, Qiang J B, Wang Y M and Dong C 2008 Co- and Fe-based multicomponent bulk metallic glasses designed by cluster line and minor alloying J. Mater. Res. 23 1543–50  
[14] Zhang Z, Cheng H, Ding D, Zhang H Y, Chen S S, Xia L and Li W H 2019 Effect of minor Nb substitution for Co on the glass forming ability and magnetic properties of the Gd50Co50 metallic glass Mater. Res. Express 6 085208  
[15] Zhao L, Z, Xue R J, Wang W H and Bai H Y 2017 LaGa-based bulk metallic glasses Chin. Phys. B 26 18106–018106
[16] Samavatian M, Gholamipour R, Samavatian V and Farahani F 2019 Effects of Nb minor addition on atomic structure and glass forming ability of Zr55Cu30Ni5Al10 bulk metallic glass Mater. Res. Express 6 065202
[17] Sohrabi S and Gholamipour R 2022 Glass transition kinetics and fragility of ZrCuAlNi(Nb) metallic glasses Intermetallics 145 107532
[18] Sharaf H K, Salman S, Abdulateef M H, Magizov R R, Troitskii V I, Mahmoud Z H, Mukhutdinov R H and Mohanty H 2021 Role of initial stored energy on hydrogen microalloying of ZrCoAl(Nb) bulk metallic glasses Applied Physics a-Materials Science & Processing. 127 28
[19] Yu D C, Geng Y, Li Z K, Liu D M, Fu H M, Zhu Z W, Qi Y and Zhang H F 2015 A new method locating good glass-forming compositions J. Alloy. Compd. 646 620–3
[20] Yu D C, Shi X G, Fu H M, Geng Y, Zhu Z W, Qi Y and Zhang H F 2015 Glass formation in Zr-Al-Fe-Cu system Mater. Lett. 157 299–302
[21] Takeuchi A and Inoue A 2005 Classification of bulk metallic glasses by atomic size difference, heat of mixing and period of constituent elements and its application to characterization of the main alloying element Mater. Trans. 46 2917–29
[22] Miracle D B 2004 Efficient local packing in metallic glasses J. Non-Cryst. Solids 342 89–96
[23] Miracle D B, Sanders W S and Senkov O N 2003 The influence of efficient atomic packing on the constitution of metallic glasses Philos. Mag. 83 2409–28
[24] Baulin O, Douillard T, Fabregue D, Perez M, Pelletier J-M and Bugnet M 2019 Three-dimensional structure and formation mechanisms of Y2O3 hollow-precipitates in a Cu-based metallic glass Mater. Des. 168 107660
[25] Wang Q 2005 Cluster line criterion and the formation of Cu-Zr(Hf)-based ternary bulk metallic glasses. Dalian Dalian University of Technology(Dalian) PhD Thesis.
[26] Lu Z P, Tan H, Li Y and Ng S C 2000 The correlation between reduced glass transition temperature and glass forming ability of bulk metallic glasses Scr. Mater. 42 667–73
[27] Lu Z P and Liu C T 2002 A new glass-forming ability criterion for bulk metallic glasses Acta Mater. 50 3501–12
[28] Du X H, Huang J C, Liu C T and Lu Z P 2007 New criterion of glass forming ability for bulk metallic glasses J. Appl. Phys. 101 132
[29] Buschow 1984 Short-range order and thermal stability in amorphous alloys J. Phys. F: Met. Phys. 14 593
[30] Kissinger H E 1957 Reaction Kinetics in Differential Thermal Analysis Anal. Chem. 29 1702–6