Original Article

Effects of similar-element-substitution on the glass-forming ability and mechanical behaviors of Ti-Cu-Zr-Pd bulk metallic glasses

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The Ti\textsubscript{44}Cu\textsubscript{36}Zr\textsubscript{10}Pd\textsubscript{13} (at.% ) metallic glasses are promising for bone-implantation applications due to their exceptional bio-compatibility. However, Pd, as a noble element, keeps the fabrication cost high and prevents the industrial sale production of these alloys. Searching for replacements with comparable glass-forming ability and ductility but lower cost turns out to be imperative. In this article, we used similar but less expensive elements to substitute Pd for such a goal. Specifically, 1-4 at.% Ni and Pt are incrementally used to replace Pd in the base alloy. Careful characterizations of the glass-forming ability and the compressive ductility suggest that the Ti\textsubscript{44}Cu\textsubscript{36}Zr\textsubscript{10}Pd\textsubscript{13}Ni\textsubscript{3} metallic glass retains both the glass-forming ability and the ductility, but cuts down the alloy cost by ∼22.66%. The Ti\textsubscript{44}Cu\textsubscript{36}Zr\textsubscript{10}Pd\textsubscript{13}Pt\textsubscript{1} metallic glass, despite no substantial trimming in the alloy cost, doubles the ductility and fairly maintains the glass-forming ability. The serrated flow is observed on the plastic flow of most metallic glasses investigated and is quantitatively studied in the framework of the self-organized criticality. Our work provides important insights on defining appropriate commercialization routes of Ti-based bulk metallic glasses.

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1. Introduction

Metallic glasses, particularly following the appearance in bulk forms, have been extensively studied over the past few decades, given their exceptional functional and structural properties, such as good electrical conductivity, high strength, large elastic limit, and excellent corrosion and oxidation resistance [1–4]. Though metallic glasses in bulk forms have been reported in numerous systems, such as Zr-, Pd-, Ti-, Fe-, Ni-, and Co-based alloys [5–10], the glass-forming ability and the limited ductility at low temperatures remain two long-standing hurdles, considerably limiting their large-scale engineering applications as a class of advanced materials [2,3]. The glass-forming ability literally refrains metallic glasses from being made into components of large sizes, and the limited ductility virtually downgrades their load-bearing capability, both placing bulk metallic glasses into a dilemma for further advancements.

In terms of glass-forming ability, Inoue’s empirical rules [11] are widely utilized as guidelines for searching for bulk metallic glasses with high glass-forming ability. The empirical rules states that an alloy would favor a glassy state when (1) it is composed of more than three types of elements, (2) atoms of major constituent elements are substantially different in size (>12%), and (3) the heat of elemental mixing presents negative values. More recent research results suggest that the glass-forming ability of bulk metallic glasses could be altered as well by partially replacing a given constituent element with similar ones. Similar elements herein refer to the neighboring elements in the periodic table. Examples in line with this principle can be found in 

\[ \text{Zr}_{55}\text{Al}_{10}\text{Ni}_{5}\text{Cu}_{30} \]

metallic glasses [12], whose critical casting diameter is brought up to 16 mm from 5 mm (the \(\text{Zr}_{50}\text{Al}_{40}\text{Cu}_{10}\) metallic glasses) after the partial substitution of Cu with Ni, and \(\text{La}_{80}\text{Ce}_{20}\text{Zr}_{40}\text{Cu}_{25}\) alloys [13], whose critical size is doubled, following the equal replacement of La with Ce in \(\text{La}_{80}\text{Al}_{10}\text{Cu}_{25}\).

Limited ductility in bulk metallic glasses is a direct macroscopic manifestation of their amorphous microstructure. Owing to the absence of cooperative plasticity-mediation mechanisms like dislocations in crystalline counterparts, shear bands tend to develop into cracks swiftly through void nucleation and coalescence [14], followed by catastrophic propagation throughout the entire sample. An express shear-band-to-crack transition essentially leads bulk metallic glasses to fail in a brittle manner in most circumstances. Extrinsically, intentionally-designed geometric constraints can help defer shear-band propagation and improve ductility through prompting the formation of denser shear bands. Preparing metallic-glass composites with nano to micro sized crystalline inclusions [9] and adopting surface modifications, such as affixing thin-film coatings [2,15], or introducing residual stresses [16,17] are two examples of many to stop shear-band propagation and improve ductility. Intrinsically, early research activities empirically advocate that the ductility of metallic glasses is correlated with their Poisson’s ratio (or equivalently the shear-to-bulk modulus ratio) [18]. After some exceptions found [19], recent works focus more on identifying a physically-meaningful microstructural parameter. Among copious concepts, the structural heterogeneity concept [3,20] is the one mostly studied, and it indeed offers a multitude of valuable insights for interpreting ductility vs. brittleness in bulk metallic glasses.

The Ti-based metallic glasses are a family of alloys of particular interest since they have promising applications in medical implants as a result of lightweight and biocompatibility attributes. However, as many other metallic glasses, the Ti-based metallic glasses, which is the focus of the present work, suffer from the same plights aforementioned. Their glass-forming ability is comparatively low with the critical size for the majority of prepared samples, limited to below 5 mm. Whilst Ti-Zr-Be-Cu-Ni [21] and Ti-Zr-Cu-Pd-Sn [10] alloys can be fabricated in a size of greater than 8 and 10 mm, respectively, both alloys are unrealistic for clinical applications. Ti-Zr-Be-Cu-Ni metallic glass contains the toxic Be; Ti-Zr-Cu-Pd-Sn metallic glasses carry the noble Pd element, which is unfavorable in the spirit of controlling cost. It is therefore necessary to explore the synthesis of low-cost and bio-friendly Ti-based metallic glasses in order to adapt for medical needs. Certainly, sufficient ductility is also a requisite for these metallic glasses to ensure a reasonably long service life. The present work attempts to use Ni and Pt to substitute the Pd element in Ti-Cu-Zr-Pd alloys for the purpose of cutting down the alloy cost by partially removing the noble element. Effects of elemental substitutions on the glass-forming ability and mechanical properties are thoroughly investigated.

2. Experimental

\[ \text{Ti}_{41}\text{Cu}_{36}\text{Zr}_{10}\text{Pd}_{13−x}\text{Ni}_{x} \] at.% \(( x = 0, 1, 2, \text{and} 3) \) and 

\[ \text{Ti}_{41}\text{Cu}_{36}\text{Zr}_{10}\text{Pd}_{13−y}\text{Pt}_{y} \] at.% \(( y = 1, 2, 3, \text{and} 4) \) alloy ingots were prepared by arc-melting constituent elements (purity > 99.9%) in argon atmosphere. Rod specimens with a diameter less than 4 mm were remelted in the quartz tube and injected into the copper mold, while those having larger diameters were remelted in the quartz cup using a tilting-induction furnace, and then poured into the copper mold. The microstructure of the prepared specimens was examined using the Bruker AXS D8 X-ray diffractometer with CuKa radiation at a scanning rate of 3°/min, and their thermal stability was characterized by a NETZSCH DSC 404C Differential Scanning Calorimeter (DSC) at a heating rate of 0.33 K/s. Compressive tests were conducted on the Sans testing machine at a strain rate of 2 \( \times 10^{-4} \) mm/s, with the specimen size of 2 mm in diameter and 4 mm in length. The fracture morphology and outer surface of the fractured specimens were examined with scanning-electron microscopy (SEM).

3. Results and discussion

3.1. Glass-forming ability

Fig. 1 gives the X-ray diffraction patterns of the base metallic glass (\(\text{Ti}_{41}\text{Cu}_{36}\text{Zr}_{10}\text{Pd}_{13}\)) and the Ni-substituted and Pt-substituted counterparts. A broad diffraction peak, a sign of an amorphous microstructure, is characteristic of all alloys but \(\text{Ti}_{41}\text{Cu}_{36}\text{Zr}_{10}\text{Pd}_{10}\text{P}_{3}\) and \(\text{Ti}_{41}\text{Cu}_{36}\text{Zr}_{10}\text{Pd}_{8}\text{P}_{2}\). The glass-forming ability of metallic glasses is herein characterized by
two out of many proposed criteria – the critical sample size that can retain an amorphous state and the width of the supercooled liquid region, $\Delta T_c = T_x - T_g$, where $T_x$ and $T_g$ are the onset temperature of crystallization and the glass-transition temperature. Table 1 lists $T_x$, $T_g$, $\Delta T_c$, and the critical diameter of rod specimens, $D_c$, of all the investigated alloys; the thermal stability data are extracted from the DSC endothermic traces in Fig. 2. The base metallic glass, Ti$_{41}$Cu$_{36}$Zr$_{19}$Pd$_{13}$, is found to have the best glass-forming ability, with a $\Delta T_c$ of 48 K and the critical sample size up to 6 mm in diameter. Substituting the Pd element with 1–3 at.% Ni tends to bring down the glass-forming ability slightly, as indicated by the mild reduction in $\Delta T_c$ and $D_c$. But given the fact that the reduction in $D_c$ is fairly small, and the unit price of the Pd element is nearly 2000 times more expensive than the Ni element, the Ni substitution of Pd can still be regarded as a beneficial act to cut down the alloy cost while sufficiently maintaining the glass-forming ability of the Ti-Cu-Zr-Pd metallic glasses. Using Pt to partially replace Pd, however, degrades the glass-forming ability substantially in most cases. As 2–4 at.% Pt is doped, the critical sample size sharply runs below 2 mm. Substituting Pd with 1 at.% Pt will lead to declined glass-forming ability too but very slightly, $D_c$ reducing from 6 mm to 4 mm. It is therefore concluded that substituting Pd with up to 3 at.% Ni or 1 at.% Pt will not impair the glass-forming ability of the Ti-Cu-Zr-Pd metallic glasses appreciably, but lower the alloy fabrication cost significantly.

Since Ni, Pt, and Pd appear in the same group of the periodic table and have the comparable atom sizes, similar valence electronic structures, and identical face-centered cubic structures in their crystalline states, the variation of the

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$x/y$</th>
<th>$T_x$ (K)</th>
<th>$T_g$ (K)</th>
<th>$\Delta T_c$ (K)</th>
<th>$D_c$ (mm)</th>
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<td>Ti$<em>{41}$Cu$</em>{36}$Zr$<em>{19}$Pd$</em>{13}$–Ni$_x$</td>
<td>0</td>
<td>696</td>
<td>744</td>
<td>48</td>
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<tr>
<td></td>
<td>1</td>
<td>665</td>
<td>708</td>
<td>43</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>666</td>
<td>708</td>
<td>42</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>694</td>
<td>736</td>
<td>42</td>
<td>4</td>
</tr>
<tr>
<td>Ti$<em>{41}$Cu$</em>{36}$Zr$<em>{19}$Pd$</em>{13}$–Pt$_y$</td>
<td>1</td>
<td>662</td>
<td>702</td>
<td>40</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>672</td>
<td>704</td>
<td>32</td>
<td>2</td>
</tr>
<tr>
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<td>3</td>
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<td>&lt;2</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>670</td>
<td>703</td>
<td>33</td>
<td>&lt;2</td>
</tr>
</tbody>
</table>
Pd element with 1 at.% Ni element drastically drops the yield strength of Ti-based alloys (~21%) and transforms the glass from moderately ductile failure to completely brittle failure. A 2 at.% Ni substitution results in a minimal deduction in yield strength but the sample still fails as soon as it overpasses yielding. Further growing the Ni content to 3 at.%, however, fairly maintains both the strength and ductility, as found in the base metallic glass. In contrast, comparing with the Ni substitution, the Pt substitution plays a remarkably disparate role, as suggested by Fig. 3(b), i.e., the plastic strain is extended twice without the deterioration of strength at Pt = 1 at.%, and both the strength and ductility are comparable to the base alloy when Pt equals 2 at.%.

Two representative metallic glasses, Ti_{41}Cu_{36}Zr_{10}Pd_{12}Ni_{1} rupturing in brittle manner and Ti_{41}Cu_{36}Zr_{10}Pd_{12}Pt_{1} failing plastically, are selected to inspect fracture characteristics for the purpose of unveiling mechanisms governing the ductility or brittle failure. The outer surfaces of the fractured specimens of these two metallic glasses are presented in Fig. 4(a) and (b), respectively. As in many other metallic glasses, quasi-static compression leads to failure in an inclined angle of 40°–46° with respect to the loading direction, hinting the co-function of the shear stress and the normal stress [27,28]. Another important feature noticed is that in the Ti_{41}Cu_{36}Zr_{10}Pd_{12}Ni_{1} metallic glass, the outer surface is nearly featureless with very few shear bands detected, but the Ti_{41}Cu_{36}Zr_{10}Pd_{12}Pt_{1} metallic glass, following the ductile fracture, exhibits an abundance of shear bands interweaving with each other. Some of them are primary while others are secondary or even lower-order branched from the upper-level ones. The magnified SEM image of the fracture surface along the major shear band in Fig. 4(b) is shown in Fig. 4(c), in which the failure features with typical vein-like patterns oriented toward the shearing direction. Moreover, many liquid-like balls are observed on the fractograph, suggesting the occurrence of local melting owing to brisk plastic dissipation [29].

It is now widely accepted that the degree of plasticity of a metallic glass is proportional to the shear band density eventually presented. Many monolithic metallic glasses fail catastrophically because all plastic strains are concentrated on a dominant shear band. Since the amount of shear strains that can be sustained by each individual shear band is limited, redistributing the plastic strain to as many shear bands as possible becomes an effective strategy for the ductility enhancement [30,31]. Likewise, the brittleness and the improved ductility in Ti_{41}Cu_{36}Zr_{10}Pd_{12}Ni_{1} and Ti_{41}Cu_{36}Zr_{10}Pd_{12}Pt_{1} metallic glasses of the current work relates as well to the denseness of shear bands. At the microscopic level, shear-banding behavior and the related ductile or brittle fracture in bulk metallic glasses is correlated with the dynamical structural heterogeneity, a concept that has ever been probed and verified by molecular dynamic simulations [32] and various experimental techniques, including high energy X-ray diffraction and anisotropic pair-density function analysis [33], statistical atomic force microscopy [34,35], dynamical micropillar compression tests [36], and instrumented indentation [3,20,37]. The conceptual model thinks of a metallic glass composed of liquid-like regions and solid-like regions. Liquid-like regions possess lower packing densities, lower moduli/hardnesses, and higher energy dissipation rates.
where the volume fraction and the viscosity of liquid-like regions [36]. The elastic spring term in Eq. (1) embodies solid-like regions, and the viscous dashpot part stands for liquid-like regions. Within this theoretical framework, W. Li et al. [3] successfully established an empirical relationship between the fracture energy density (a quantitative measure of the brittleness or the ductility of a material) and the density of structural heterogeneities, in the exponential form of

\[ E = c_1 \exp(c_2\rho_{def}) \]  (2)

where \( E \) is the fracture energy density, \( \rho_{def} \) is the density of structural heterogeneities, and \( c_1 \) and \( c_2 \) are empirical constants.

In light of this theory, the varied brittle and ductile mechanical behaviors of the Ti-based metallic glasses after substituting Pd with 1–3 at.% Ni or Pt is most likely to be attributable to the fluctuation in the density of structural heterogeneities. The change in the quantity of structural heterogeneities, on the other hand, roots in the alternation of icosahedral clusters. As discussed in Section 3.1, the variously reduced glass-forming ability in Ni- and Pt-substituted Ti-based metallic glasses is presumably caused by the declining density of icosahedra-like atomic clusters due to the intrusion of Ni and Pt elements [33–25]. Besides, icosahedra-like clusters also serve as the atom-level source of structural heterogeneities [32], and the reduction in their density by the disturbance of Ni and Pt elements induces metallic glasses to transit from being modest ductile to utterly brittle. This rationale, however, finds the exception in the TiCu36Zr10Pd12Pt1 alloy, whose glass-forming ability is slightly reduced but ductility is enhanced compellingly. This trend simply implies that the ductility of metallic glasses might be mandated by factors other than icosahedra clusters. Further investigation on this trend is need.

### 3.3. Serrated plastic flow

The plastic flow of metallic glasses subjected to uniaxial loading universally exhibits serrated behavior, i.e., the stress rises and drops in a cyclic and discontinuous manner. Likewise, the serrated flow is observed for most Ti-based metallic glasses studied presently, as shown in Fig. 3. The detailed examination of the serrated plastic flow for three representative metallic glasses, TiCu36Zr10Pd13, TiCu36Zr10Pd12Pt1, and Ti41Cu36Zr10Pd12Pt1, is provided in Fig. 5, in which each plot is an enlarged view of the enclosed box on the corresponding curve in Fig. 3. Dissecting Figs. 3 and 5 jointly suggests the subdivision of the serrated flow into two regions: in the region I, each cycle starts with an abruptstress shock of high magnitudes, followed by several aftershocks of smaller magnitudes; in the region II, smaller aftershocks become absent and each cycle of stress shock only contains the major one and some slight vibration originating from the testing fixture [38]. The two-region feature in the serrated flow is reminiscent of the self-organized criticality (SOC), a property commonly existing in complex dynamical systems [39,40]. The smaller serration events in the region I signifies an apparent SOC behavior of metallic glasses in response to dynamically fluctuated loads.

**Fig. 4** – The fracture surfaces of (a) the Ti41Cu36Zr10Pd12Ni1 metallic glass and (b) the Ti41Cu36Zr10Pd12Pt1 metallic glass, along with (c) the high magnification view of the shearing surface in (b) showing typical vein patterns and melting balls.
With an intention of withdrawing more useful information from the serrated plastic flow, stress drops in all metallic glass samples but the brittle Ti$_{41}$Cu$_{36}$Zr$_{10}$Pd$_{13}$Ni$_{1}$ are extracted and plotted in Fig. 6 against time. The complementary cumulative probability of the stress drops shown in Fig. 7 is fitted using a power-law distribution accompanied by a squared exponential decay function [38]

$$\text{CCDF} = A\Delta S^{-\beta}\exp\left[-\left(\frac{\Delta S}{S_c}\right)^2\right]$$  

(3)

where $A$ is the normalization constant, $\beta$ is the scaling exponent, and $S_c$ is the cut-off drop stress. Since it is widely recognized that serration events observed in metallic glasses are a manifestation of the shear-banding events going on at the micro-scale, the fitting parameters in Table 2 obtained through Eq. (3) are expected to offer useful fingerprints on dynamics of shear-banding events. The $\beta$ values for five metallic glasses vary only in a very narrow range, quantitatively confirming the SOC behavior of the serrated flow, in agreement with Wang et al. [38]. The SOC behavior features systems having a characteristic ($\beta$), independent of chemical composition, plastic strain, yield stress, and so forth [38]. $S_c$ is the cut-off drop stress, beyond which the squared exponential decay term comes into play. Its values for each metallic glass withdrawn from Eq. (3) fitting is marked in the corresponding graph of Fig. 7 and plotted against the plastic strain in Fig. 8. Generally, $S_c$ decreases with the increasing plasticity in a nonlinear way, as opposed to the cut-off elastic energy density studied in the same way in Ref. [38]. Since the elastic strain energy is a multiplication of the stress and strain, the current finding is indicative that the cut-off burst strain positively relates with the plasticity, whereas, the cut-off drop stress negatively correlates with the plasticity in metallic glasses.

4. Summary

In summary, our exploration of using similar but less or comparatively expensive elements to partially substitute the noble element Pd in the Ti$_{41}$Cu$_{36}$Zr$_{10}$Pd$_{13}$ metallic glass yields the findings as follows.

(i) Substituting Pd with 3 at.% Ni retains both the glass-forming ability and the compressive ductility found in the base metallic glass, but cuts down the alloy fabrication cost by ~22.66%. The 1–2 at.% Ni substitution, on the other hand, yields embrittlement in metallic glasses though the comparative glass-forming ability can be preserved.

(ii) Pt and Pd have comparable unit prices. Substituting Pd with 1 at.% Pt doubles the compressive ductility and also maintains the glass-forming ability relative to the base alloy. The 2 at.% Pt substitution leads to both the significantly degraded glass-forming ability and ductility. As the Pt substitution is in excess of 2 at.%, apparent crystallization begins precipitating.

(iii) Considering the fabrication cost, glass-forming ability, and ductility, the Ti$_{41}$Cu$_{36}$Zr$_{10}$Pd$_{13}$Ni$_{1}$ metallic glass will be the first priority replacement of the Ti$_{41}$Cu$_{36}$Zr$_{10}$Pd$_{13}$ metallic glass followed by Ti$_{41}$Cu$_{36}$Zr$_{10}$Pd$_{13}$Pt$_{1}$. The

These multiple stress undulations tend to drive the system to dynamically self-organize to a new critical state. The gradual absence of the smaller serrations as the flow enters the region II, on the other hand, is an implication of the decaying self-organization behavior.

Fig. 5 – The enlarged view of the serrated flow in (a) the Ti$_{41}$Cu$_{36}$Zr$_{10}$Pd$_{13}$ base metallic glass, (b) the Ti$_{41}$Cu$_{36}$Zr$_{10}$Pd$_{13}$Pt$_{1}$ metallic glass, and (c) the Ti$_{41}$Cu$_{36}$Zr$_{10}$Pd$_{13}$Pt$_{2}$ metallic glass at the corresponding enclosed box in Fig. 3.
Fig. 6 – The stress drop as a function of time for (a) Ti_{41}Cu_{36}Zr_{10}Pd_{13}, (b) Ti_{41}Cu_{36}Zr_{10}Pd_{11}Ni_{2}, (c) Ti_{41}Cu_{36}Zr_{10}Pd_{10}Ni_{3}, (e) Ti_{41}Cu_{36}Zr_{10}Pd_{12}Pt_{1}, and (e) Ti_{41}Cu_{36}Zr_{10}Pd_{11}Pt_{2}.

Fig. 7 – The complementary cumulative distribution of the stress drop for (a) Ti_{41}Cu_{36}Zr_{10}Pd_{13}, (b) Ti_{41}Cu_{36}Zr_{10}Pd_{11}Ni_{2}, (c) Ti_{41}Cu_{36}Zr_{10}Pd_{10}Ni_{3}, (e) Ti_{41}Cu_{36}Zr_{10}Pd_{12}Pt_{1}, and (e) Ti_{41}Cu_{36}Zr_{10}Pd_{11}Pt_{2}. Red dashed lines indicate the cut-off drop stress, S_c, attained from Eq. (3) fitting.
Table 2 - The plastic strain and fitting parameters in Eq. (3) for the base metallic glass, Ti$_{41}$Cu$_{36}$Zr$_{10}$Pd$_{13}$, and the Ni- and Pt-substituted metallic glasses.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>x/y</th>
<th>Plastic strain (%)</th>
<th>A</th>
<th>β</th>
<th>S$_c$ (MPa)</th>
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<tr>
<td>Ti$<em>{41}$Cu$</em>{36}$Zr$<em>{10}$Pd$</em>{13}$-Ni$_{3}$</td>
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<td>6</td>
<td>2.0</td>
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<td>3</td>
<td></td>
<td>4.2</td>
<td>0.51</td>
<td>91.1</td>
</tr>
<tr>
<td>Ti$<em>{41}$Cu$</em>{36}$Zr$<em>{10}$Pd$</em>{13}$-Pt$_{1}$</td>
<td>1</td>
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<td>6.3</td>
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<td>2.7</td>
<td>0.35</td>
<td>70.7</td>
</tr>
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</table>

Fig. 8 - The cut-off drop stress extracted from fitting Eq. (3) to Fig. 7 as a function of the compressive plastic strain. The trend line shown is for visual guide.

Ti$_{41}$Cu$_{36}$Zr$_{10}$Pd$_{13}$Ni$_{3}$ metallic glasses can be considered for potential large-scale production, while Ti$_{41}$Cu$_{36}$Zr$_{10}$Pd$_{13}$Pt$_{1}$ can meet some special needs in which superior plasticity is required.

(iv) Statistical analysis of the serrated flow in the investigated metallic glasses suggests the self-organized criticality behavior. The cut-off drop stress is positively correlated with the plasticity, whereas the cut-off burst stress is negatively correlated.

Conflicts of interest

The authors declare no conflicts of interest.

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