J MATER RES TECHNOL. 2017;xxx(xx):xxx–xxx

Available online at www.sciencedirect.com

jmr&t Journal of Materials Research and Technology

www.jmrt.com.br

Original Article

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

*Haoling Jia*[a,b], *Xie Xie*[b], *Lei Zhao*[a], *Jianfeng Wang*[c], *Yanfei Gao*[b,d], *Karin A. Dahmen*[e], *Weidong Li*[b,*], *Peter K. Liaw*[b,*], *Chaoli Ma*[a,*]

[a] *Department of Materials Science and Engineering, Beihang University, Beijing 100083, China*
[b] *Department of Materials Science and Engineering, The University of Tennessee, Knoxville, TN 37996, USA*
[c] *School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, China*
[d] *Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA*
[e] *Department of Physics, University of Illinois at Urbana Champaign, Urbana, IL 61801, USA*

ARTICLE INFO

*Article history:*
Received 27 June 2017
Accepted 19 August 2017
Available online xxx

*Keywords:*
Glass forming ability
Plasticity
Serrated flow
Self-organized criticality

ABSTRACT

The $Ti_{41}Cu_{31}Zr_{10}Pd_{13}$ (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 $Ti_{41}Cu_{36}Zr_{10}Pd_{10}Ni_3$ metallic glass retains both the glass-forming ability and the ductility, but cuts down the alloy cost by ~22.66%. The $Ti_{41}Cu_{36}Zr_{10}Pd_{12}Pt_1$ 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.



* *Corresponding author.*
E-mails: lei432378yu@gmail.com (W. Li), pliaw@utk.edu (P.K. Liaw), clma2001@gmail.com (C. Ma).

http://dx.doi.org/10.1016/j.jmrt.2017.08.009

## 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 of 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 $Zr_{55}Al_{10}Ni_5Cu_{30}$ metallic glasses [12], whose critical casting diameter is brought up to 16 mm from 5 mm (the $Zr_{50}Al_{10}Cu_{40}$ metallic glasses) after the partial substitution of Cu with Ni, and $(La_{0.5}Ce_{0.5})_{65}Al_{10}Cu_{25}$ alloys [13], whose critical size is doubled, following the equal replacement of La with Ce in $La_{65}Al_{10}Cu_{25}$.

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. Such 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

$Ti_{41}Cu_{36}Zr_{10}Pd_{13-x}Ni_x$ at.% (x = 0, 1, 2, and 3) and $Ti_{41}Cu_{36}Zr_{10}Pd_{13-y}Pt_y$ at.% (y = 1, 2, 3, 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 CuKα 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 $2 \times 10^{-4}$ m/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 ($Ti_{41}Cu_{36}Zr_{10}Pd_{13}$) and the Ni-substituted and Pt-substituted counterparts. A broad diffraction peak, a sign of an amorphous microstructure, is characteristic of all alloys but $Ti_{41}Cu_{36}Zr_{10}Pd_{10}Pt_3$ and $Ti_{41}Cu_{36}Zr_{10}Pd_9Pt_4$. The glass-forming ability of metallic glasses is herein characterized by

Please cite this article in press as: Jia H, et al. Effects of similar-element-substitution on the glass-forming ability and mechanical behaviors of Ti-Cu-Zr-Pd bulk metallic glasses. J Mater Res Technol. 2017. http://dx.doi.org/10.1016/j.jmrt.2017.08.009