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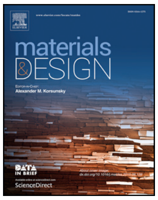

Gradient microstructure with martensitic transformation for developing a large-size metallic alloy with enhanced mechanical properties

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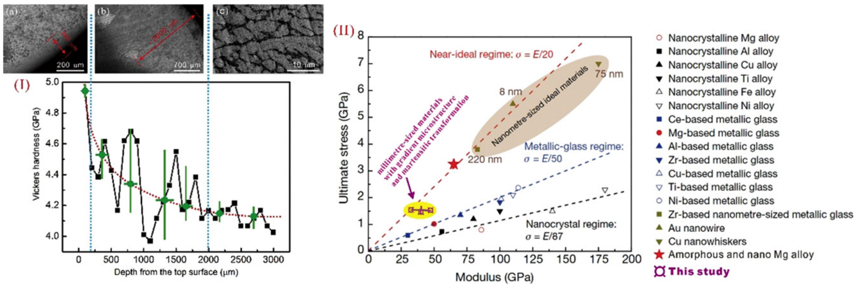
HIGHLIGHTS

- A 7 mm-diameter $Zr_{48}Cu_{48}Al_4$ alloy rod is architectured by a fast cooling rate technology.
- Gradient microstructure is related to both phase and grain size.
- Martensitic transformation also occurs, responding to an applied loading.
- The low modulus, fast strain hardening and high strength of the metallic alloy rod are characterized.
- The designing concept in this work will guide the high-performance material development.

GRAPHICAL ABSTRACT

Optimization in microstructure and mechanical properties of the 7 mm-diameter metallic alloy rod: (I) gradient microstructure with martensitic transformation, consisting of amorphous and nano ZrCu phases in top surface layer, fine-grained ZrCu, Zr_2Cu and $Cu_{10}Zr_7$ phases in subsurface layer, and coarse-grained Zr_2Cu and $Cu_{10}Zr_7$ phases in center region; (II) ultimate stress plotted against Young's modulus showing that the strength-modulus relation nearly lies in the regime of the ideal materials which is far from the regimes of metallic glasses and nanocrystallines.



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ABSTRACT

This work presents the development of a large-size metallic alloy rod with low modulus, fast strain hardening and high strength through designing the gradient microstructure with martensitic transformation. The gradient microstructure is revealed in both phases and grain sizes, which consists of amorphous and nano ZrCu phases in the top surface, fine-grained ZrCu, Zr_2Cu and $Cu_{10}Zr_7$ phases in the subsurface, and coarse-grained Zr_2Cu and $Cu_{10}Zr_7$ phases in the center. Hardness in the cross section of the metallic alloy rod shows a decreasing tendency from the top surface to center. Compressive mechanical tests illustrate an initial linear elastic deformation to yielding, followed by a fast strain hardening to the final fracture. Strain delocalization process accompanying with martensitic transformation is supposed to take place progressively in the gradient microstructure, which contributes to the performance of low modulus, fast strain hardening and high strength. Shearing fracture model with shear banding, nano wrinkling and micro cracking is revealed, which indicates the mixed mechanical behavior of ductile and brittle models. Gradient microstructure with martensitic transformation is impressive for developing the large-size metallic alloys with low modulus, fast strain hardening and high strength.

1. Introduction

High-strength design is a long-term research target for optimizing the materials and material structures [1–6]. Also, toughening performance is important for undertaking the high-level applied loading without a catastrophic fracture. One of the valid methods of improving

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the strength of a metallic material is decreasing grain size, which leads to the emergence of ultrafine-grained and nanocrystalline materials [1,2,6,7]. When grain size is reduced nearly into zero, material microstructure becomes disordered, which is the formation of amorphous alloys [5]. Amorphous alloys have attracted a great attention in science and engineering, because of their excellent strength and elasticity [8,9]. Generally, the small-scale amorphous alloys have the enhanced mechanical properties [10–12]. However, when material size is increased, structural relaxation or/and brittle phase precipitation will occur, which extensively deteriorates the mechanical performance [5,8]. Such a deterioration of mechanical performance caused by the increase of material size will significantly impede the application in structural engineering.

Optimizing the mechanical properties of the large-size amorphous alloys via the additional phases is very important for the engineering application. Recently, martensitic transformation has become a hot research topic prevailing in (Zr,Cu)-based metallic alloy, which has an important effect on the mechanical performance of the large-size materials [13–23]. (Zr,Cu)-based metallic alloy exhibits two main unique characteristics of that (1) the binary Zr-Cu melts can solidify into amorphous phase, displaying a good glass forming ability (GFA) [17,18,21,23]; and (2) the equiatomic ZrCu (B2) austenitic phase can undergo a martensitic transformation from a cubic primitive B2 phase (Pm-3 m) to two monoclinic (Cm and P21/m) phases, showing phase-transformation-induced plasticity with a high strength and fast strain hardening [16,22,24–26]. Such the mechanisms can make a more homogeneous plastic deformation with strain hardening, and the local stress concentration can be suppressed [22,23,26]. However, ZrCu is a metastable phase at high temperature, which tends to decompose into brittle Zr_2Cu and $Cu_{10}Zr_7$ phases via a eutectoid reaction at a temperature of about 988 K [22,23].

In this study, for precipitating the amorphous and ZrCu (B2) austenitic phases, the component of $Zr_{48}Cu_{48}Al_4$ in atom ratio, together with a fast cooling rate technology, is employed. The addition of minor Al element is for improving the glass forming ability (GFA) and for a positive influence on phase transformation [27]. A large-size metallic alloy rod with 7 mm diameter is developed with gradient distribution in microstructure. Due to the increase of cooling rate from the center to top surface, amorphous and nano ZrCu (B2) austenitic phases are expected to be precipitated in the top surface, and with the increase of depth, the nano ZrCu (B2) austenitic phase will grow and decompose into the coarse grained Zr_2Cu and $Cu_{10}Zr_7$ intermetallics in the center region. Thus, the gradient microstructural distribution in both phase and grain size including ZrCu (B2) austenites is architectured, which is supposed to contribute to the low modulus, fast strain hardening and high strength of the metallic alloy rod, considering the gradient strength distribution according to the Hall-Petch equation [28–31]. It is meaningful to develop a high-performance large-size metallic alloy for the innovations in material sciences.

2. Experimental methods

Alloy ingots with the nominal compositions of $Cu_{48}Zr_{48}Al_4$ (at.%) were prepared by arc melting the pure metallic mixtures of ultrasonically cleansed Zr (99.9 at.%), Cu (99.99 at.%) and Al (99.99 at.%) pieces under a Ti-gettered high-purity argon atmosphere. To ensure chemical homogeneity, each ingot was flipped and re-melted five times with electromagnetic stirring by adding a current loop under the copper crucible, and then was cooled to room temperature via suction casting into a fast water-cooled copper mold. As-cast metallic alloy rods are cylindrical with 7 mm diameter and 80 mm length.

Gradient microstructure and phases distribution at different locations of the as-cast cylindrical metallic alloy rod were revealed by X-ray diffraction (XRD) using the diffractometer equipped with a Cu-Ka radiation. Transmission electron microscopy (TEM JEM 2010) operated at 200 kV was used to analyze the microstructure in the top surface layer of the metallic alloy rod. Vickers hardness tests were operated with the load of 100 g for 10s from the top surface (100 μm) to center (3000 μm) of the metallic alloy rod. The measurement was conducted on the cross section of a cylindrical specimen, which is thick enough for avoiding the occurrence of cutting through the tested specimen during Vicker's hardness test. At each location with a certain depth, 2–3 points are tested and the average data are calculated as the final hardness value. Optical microscopic (OM) observations on the cross section of the metallic alloy rod were conducted after being etched by hydrofluoric acid.

Quasi-static uniaxial compression tests were carried out on the specimens with 7 mm diameter and 7 mm length by using a computer-controlled SUNS CMT 5105 material test machine at nominal strain rates of 1×10^{-4}/s and 1×10^{-2}/s at room temperature. Herein, the effect of frame stiffness is avoided by using a test machine with the high stiffness and maximum loading [32]. Also, the effect of aspect ratio is considered and the specimens with uniform size are used [33]. At each strain rate, three-times tests were conducted for confirming the repeatability and reliability of the mechanical data. After compression tests, the deformation and fracture behaviour as well as the toughening mechanisms are analyzed by a field-emission scanning electron microscopy (SEM). The low modulus, fast strain hardening and high strength of this gradient metallic alloy is illustrated.

3. Results and discussions

3.1. Gradient microstructure

Fig. 1 shows the XRD patterns of the as-cast $Zr_{48}Cu_{48}Al_4$ metallic alloy rod recorded at different locations. The diffraction peaks, recorded in the cross sectional area, can be identified as a mixture of amorphous, ZrCu, $Cu_{10}Zr_7$ and Zr_2Cu phases. The ZrCu phase has a maximum fraction which will occur to martensitic transformation subjected to an applied loading [16]. The dominant diffraction peaks, recorded on the top surface, are recognized as amorphous and nano ZrCu phases, which are similar with the report in Refs. [13,20].

To further shed light on the microstructure in the top surface layer, transmission electron microscopy (TEM) is employed to examine the specimen, as shown in Fig. 2. The bright-field TEM image clearly exhibits a homogeneous distribution of the nano crystalline ZrCu phases inside the amorphous matrix (see Fig. 2(a)). The corresponding selected-area electron diffraction (SAED) pattern consists of the spotty diffraction rings with a diffuse background, as shown in the inset. The average

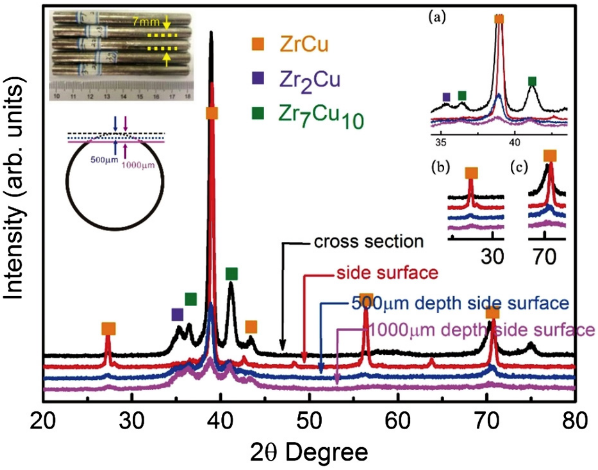

Fig. 1. XRD patterns of the as-cast $Zr_{48}Cu_{48}Al_4$ alloy rod with 7 mm diameter and 80 mm length, revealing the gradient distribution in microstructure of the precipitated amorphous, ZrCu, $Cu_{10}Zr_7$ and Zr_2Cu phases at different locations. The insets of (a), (b) and (c) show the decrease of the diffraction peak of ZrCu phase indicating its decomposition into $Cu_{10}Zr_7$ and Zr_2Cu phases with the increase of depth.