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Hierarchical nanoporous metal/BMG composite rods with excellent mechanical properties

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ABSTRACT

Hierarchical nanoporous structured NPC/BMG composite rods (NPC/BMG: nanoporous copper/bulk metallic glass) were facilely fabricated by one-pot chemical dealloying the $Cu_{50}Zr_{45}Al_5$ BMG rods in 0.05 M HF solution for 24 h. The cross-sectional SEM images illustrate that the NPC/BMG composite rods exhibit the perfect combination of inner rod-shaped Cu-Zr-Al amorphous phase core and outer tube-shaped NPC layer with a thickness of 85 μm. As compared to the reported NPC composites, the new composite rods demonstrate remarkable enhanced mechanical properties with an ultrahigh strength of 1500 MPa and a large compression strain of 2.9%. Additionally, the increase in the compression strain is attributed to the formation of the buffer deformation zone resulting from the existence of the outer nanoporous copper tube.

1. Introduction

Nanoporous metals (NPMs) obtained by facile dealloying process [1–5] have attracted considerable attention in recent years due to their superior properties and potential as new functional materials [6–9]. However, these nanoporous metals are mainly fabricated in the form of thin ribbons or films and cannot well achieve good mechanical properties, which could easily cause crush and collapse in engineering application with their inherent brittleness. Since then, great efforts have been devoted to the development of macro-scale nanoporous metals [10–12] and bulk nanoporous-composites [13,14] with high mechanical properties. The synthesis of millimeter-sized bulk hierarchical NPC via dealloying the crystalline Al-Cu alloy has been studied [12] and the bulk NPC showed a compressive strength of 5.8 MPa. It is noteworthy that the fracture strength of the monolithic nanoporous metals has been restricted by the fragile ligament structure. So, it is necessary to fabricate a new-type of nanoporous composites for breaking this limitation to achieve a superior level. Recently, the centimeter-sized NPG-based composites combined with polymer component, possessing a large ductility and an appreciable strength excess of 100 MPa, has been developed by Wang et al. [13]. However, the complex fabrication steps prolonged the production time and increased the cost of materials. Therefore, studying a facile synthesis of large-sized NPMs with excellent mechanical properties is urgently needed for their further applications. Owing to the chemically homogeneous single-phase nature, absence of crystalline defects as well as high strength, the $Cu_{50}Zr_{45}Al_5$ bulk metallic glass (BMG) rod with compressive strength of 2000 MPa [15–17] is chosen as the dealloying precursor to fabricate a new-type of NPC/BMG composite rods (NPC/BMG: nanoporous copper/bulk metallic glass) via one-step dealloying method in HF solution. The new NPC/BMG composite alloy with excellent mechanical properties and hierarchical nanoporous structure is very promising as a new advanced material.

2. Experimental methods

An alloy with nominal composition of $Cu_{50}Zr_{45}Al_5$ (at.%) was prepared by arc-melting elemental Cu, Zr and Al of 99.99 mass% purity in a Ti-gettered argon atmosphere. Bulk metallic glasses in a rod form, with a diameter of 2 mm and a length of 50 mm, were produced by an injection copper mold casting method. Dealloying

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was performed in 0.05 M HF in a free corrosion condition, open to air at 298 K. The X-ray diffractions of the as-cast and as-dealloyed rods were collected using Cu Kα radiation. The microstructure and morphology of the as-dealloyed specimens were examined by scanning electron microscopy (SEM, Hitachi S-4800, 15 keV) equipped with an X-ray energy dispersive spectroscope (EDS). Mechanical properties were measured with an Instron mechanical testing machine and an Electronic Instruments strain gauge for the sample with gauge dimensions 4 mm long and 2 mm diameter. The strain rate was $5.0 \times 10^{-4}\ s^{-1}$.

3. Results and discussion

3.1. Fabrication and microstructure of NPC/BMG composite rod

To fabricate the NPC composites with high mechanical properties, the $Cu_{50}Zr_{45}Al_5$ BMG rods with a diameter of 2 mm is subjected to the dealloying in 0.05 M HF solution for 24 h at 298 K. The optical photo and the XRD patterns of the as-cast $Cu_{50}Zr_{45}Al_5$ alloy rods before and after dealloying are shown in Fig. 1. From Fig. 1a, it can be clearly seen that the color of the rods after dealloying in HF for 24 h changes from argentous to a typical Cu metallic luster. In addition, the XRD pattern (Fig. 1b) of the as-cast $Cu_{50}Zr_{45}Al_5$ rod exhibits a broad diffraction halo without any distinguishable crystalline Bragg peak, indicating the formation of fully amorphous structure. After dealloying, it is identified that a broad amorphous halo peak is superimposed with the sharp diffraction peaks of fcc Cu and minor Cu_2O crystalline phase. This result shows that fcc Cu metal is formed on the glassy matrix by selectively removing the Zr and Al elements in HF solution [18], demonstrating that nanoporous copper plus BMG matrix (NPC/BMG composite rod) is produced by dealloying in 0.05 M HF solution for a proper time.

Fig. 2a shows the cross sectional morphology of the NPC/BMG composite rod. It is interestingly seen that the NPC tubular layer (marked by red color) with a uniform thickness of 85 μm covers evenly on the BMG matrix rod. In addition, the NPC tubular layer has a good interface combination with the BMG matrix. In order to observe the change in the surface morphology and microstructure with dealloying depth of the NPC/BMG composite rod, we carefully peeled off the immersed alloy surface layer by layer. Fig. 2b and c shows the dealloyed microstructure along the depth for the $Cu_{50}Zr_{45}Al_5$ BMG rods immersed in 0.05 M HF solution for 24 h. After peeling, it is found that the dealloyed alloy exhibits a hierarchical architecture with different channel/ligament size distributions upon the dealloying depth (A-layer: outer layer, B-layer: beneath A-layer, C-layer: beneath B-layer, and D-layer: inner layer). Fig. 2d and e represent SEM images at higher magnifications with their corresponding EDS results taken from the region A and B, respectively, in Fig. 2b. From the both EDS spectra, the elemental compositions of the porous surfaces mainly consist of Cu, verifying that the porous surfaces covering on the BMG matrix are nanoporous copper (NPC). Apparently, the NPC (Fig. 2b–e) exhibits an open, interpenetrating and three dimensional (3D) ligament-channel structure. It is worth noting that there are the ligament width and nanopore size gradient through the whole NPC depth, as plotted in Fig. 2f. The nanopore size gradually increases from 45 nm at A-layer to 72 nm at C-layer, whereas the ligament width decreases from 118 nm at A-layer to 60 nm at C-layer. Moreover, the SEM-EDS line-scan profile of Zr, Al and Cu elements sweeping from the amorphous matrix (D-layer) to the NPC (C-layer) is inserted in Fig. 2c. The results further confirm that the dealloying process results in selective dissolution of Al and Zr elements and the self-assembly of the residual Cu atoms. On the other hand, from Fig. 2c, it is clearly observed that many corrosion pits caused from the constituent elements Zr and Al in the alloy are formed on the inner glassy matrix (D-layer), which is believed to be the initial origin for forming NPC [19]. The cross sectional morphology and the dealloyed microstructure along the depth for the composite rod are schematically illustrated in Fig. 2g. The possible formation mechanism of the hierarchically structured NPC tubular layer can be proposed from two aspects. Firstly, unlike a thin film and thin ribbon precursor, the dealloying of a BMG rod with a diameter of 2 mm starts from the outer surface and gradually evolves to the inner layer, which causes a large time interval of dealloying between the inner and outer layer of the BMG rod. Thus, the early formed ligaments of NPC at outer part become ripening and coarsening, whereas the fresh NPC at inner part is just formed. Secondly, because the Cu, Zr and Al constituent elements in HF solution exhibit different atomic diffusivity and chemical reactivity, the dealloying process results in the composition gradient and fluctuation along the depth of the rod sample which gives rise to the change in the ligament/pore sizes from the outer layer to the inner layer. As a result, the new-type of NPC/BMG composite rod with hierarchical nanoporous copper covering on the BMG matrix has been synthesized successfully by immersion the $Cu_{50}Zr_{45}Al_5$ BMG rod in 0.05 M HF solution for 24 h.

3.2. Mechanical properties of the NPC/BMG composite rod

Fig. 3 shows compressive stress-strain curves of the as-cast 2 mm diameter $Cu_{50}Zr_{45}Al_5$ BMG rod and the NPC/BMG-composite rod in uniaxial compression at room temperature. The

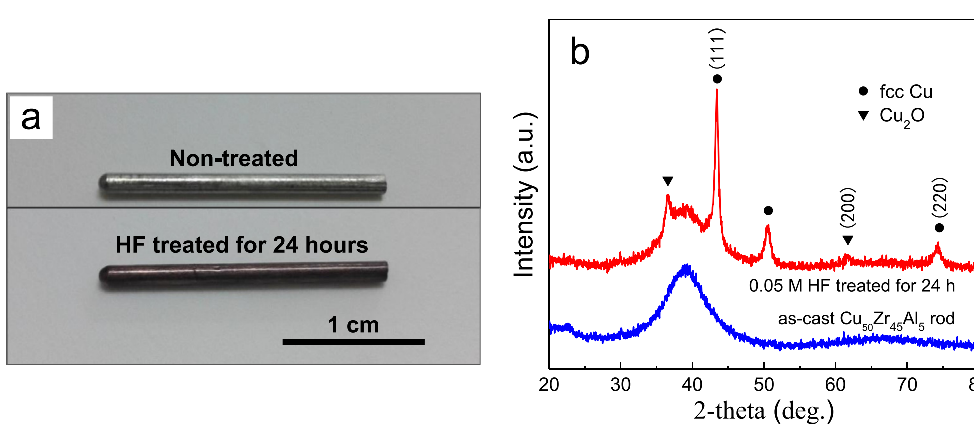

Fig. 1. (a) Photos (scale bar, 1 cm) and (b) XRD patterns of the as-cast $Cu_{50}Zr_{45}Al_5$ rods before and after dealloying in 0.05 M HF for 24 h at 298 K.