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Dealloying-based metal-polymer composites for biomedical applications

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ABSTRACT

Here, we developed interpenetrating-phase metal-polymer composites mimicking mechanical behavior of cortical bone and occupying previously unclaimed region at the Ashby diagram in the area of intermediate strength and low stiffness. The composites consist of dealloying-based open porous Ti_xHf_{100-x} alloys (scaffolds) impregnated by polymer. The scaffolds significantly contribute to strength (215–266 MPa) and stiffness (15.6–20.8 GPa) of the composites while the polymer phase provides their high strain rate sensitivity (0.037–0.044). Tuning scaffolds' connectivity by preloading and/or their chemical composition allows fine optimization of composites' mechanical properties. The results suggest that the composites may provide a basis for promising future implant materials.

Metallic materials, such as titanium alloys, are widely used for bone trauma healing, because of their good mechanical performance, excellent biocompatibility, and high corrosion resistance [1–3]. Despite the success of existing implant materials in many cases, there is a risk of bone degeneration and implant loosening caused by the "stress-shielding" effect [2,3]. The "stress-shielding" effect is associated with a disproportional load distribution between a bone and an adjacent implant due to their stiffness mismatch. The metallic implant materials are usually considerably stiffer as compared to bones. Eventually, the stiffness mismatch may lead to bone resorption and loosening or failure of implant. Effective strategies to develop low stiffness titanium alloys include development of highly alloyed beta titanium alloys [4–6], designing of complex nano-/microstructures [7–10] and fabrication of porous alloys [11–13]. Recently, it was reported that infiltration of porous alloys by polymers can lead to mechanical properties attractive for biomedical applications [13]. In latter case, the open porous alloys were synthesized by liquid metal dealloying.

The liquid metal dealloying (LMD) as proposed by Kato and coworkers [14] is a metallurgical process for synthesis of porous materials by means of selective corrosion in a liquid metal. It employs diffusion of a liquid metal into a precursor material accompanied by selective dissolution of one/several components. The remaining part of the precursor material is immiscible with the liquid metal and rearranges into a continuous scaffold consisting of interconnected ligaments. The size of ligaments of the dealloying-based materials can be tuned from the nano- to the micrometer range by control of processing conditions [13,15–18]. Currently, a wide range of porous metals, including Ti [13,14], Fe [19], Zr [13], Cr [19], Nb [16], Ta [20], TiNb [13], TiZr [13], hierarchically-structured Fe-based alloy [21], were developed by LMD. Moreover, LMD was reported to be effective in surface modification for bio-applications, e.g. patterning of tailorable nanotopographies [22] and selective removal of toxic elements [23]. The interpenetrating-phase materials by LMD offer novel opportunities for load-bearing applications [24] as well as fabrication of advanced implant materials [13].

Here, we report on the synthesis and structure-property correlation of titanium hafnium open porous alloys (Ti_xHf_{100-x} scaffolds) and interpenetrating-phase composites obtained by impregnation of the Ti_xHf_{100-x} scaffolds by bisphenol F epoxy resin. The Ti-Hf alloys were selected for this study because of good biocompatibility and osteoconductivity of both Ti and Hf [25]. Furthermore, an addition of Hf to Ti gradually increases strength of Ti-Hf alloys due to solid solution strengthening [26]. Synthesized by dealloying in liquid Mg, the Ti_xHf_{100-x} scaffolds inherit a unique microstructure through manufacturing leading to its outstanding mechanical properties. The mechanical properties of the Ti_xHf_{100-x} scaffolds are tunable through preloading treatments providing an opportunity for precise stiffness adjustment between implant and bone. The impregnation of the Ti_xHf_{100-x} scaffolds by polymer leads to their significant strength improvement. The yield strength of the metal-polymer composites exceeds that of cortical bone while its stiffness matches that of bone. Moreover, the composites exhibit high strain rate sensitivity similar to bone.[1] These findings suggest advantages of the dealloying-based composites for biomedical applications as bioimplants with adjustable mechanical properties.

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[1] The strain rate values of bone were derived from the stress-strain curves tested at different strain rates by Crowninshiled and Pope [34].

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The design of precursor alloys for LMD was based on the enthalpy of mixture between Mg and the considered alloy element ($\Delta H^{mix}_{(Mg\,-\,element)}$) as well as on biocompatibility of the alloying elements. Elements exhibiting a negative value of $\Delta H^{mix}_{(Mg\,-\,element)}$ like Cu are miscible and will be dissolved in Mg upon the dealloying process while those possessing a positive $\Delta H^{mix}_{(Mg\,-\,element)}$ like Ti and Hf are immiscible in Mg. Thus, Ti, Hf and Cu were selected for the alloy design, because these elements are miscible with each other [27]. Three alloys, namely, $Ti_{20}Hf_{20}Cu_{60}$, $Ti_{25}Hf_{15}Cu_{60}$, and $Ti_{30}Hf_{10}Cu_{60}$ (at.%) were designed in order to identify the effect of Hf on microstructure and mechanical response of the porous Ti_xHf_{100-x} alloys.

The samples (rods of 1 mm in diameter) for LMD were prepared from pure metals (99.99%) by a suction casting set-up under argon atmosphere. The rods were cut to 1.7 mm length by a diamond wire saw and dealloyed at 1023 K for 600 s in Mg in a glassy carbon crucible under argon flow using an infrared furnace (IRF 10, Behr, Switzerland). Upon dealloying, molten Mg selectively dissolves Cu out of the parent $(Ti_xHf_{100-x})_yCu_{100-y}$ alloys, while Ti and Hf diffuse along the metal/liquid interface [14,20]. To obtain porous samples, the Mg phase was removed by etching in 3 M HNO_3. The composites were prepared by subjecting the porous metal samples to vacuum for 10 min and then bringing them in contact with the liquid Bisphenol F epoxy resin (BER 20, Buehler, Germany, number average molecular weight ≤ 700 g mol^{-1}) mixed 4:1 with amine hardener (BEH 20, Buehler), using a vacuum impregnation unit (CitoVac, Struers, Germany). The detailed experimental procedure is described in [13].

As detailed above, mm-sized open porous Ti_xHf_{100-x} samples were fabricated by dealloying of the $(Ti_xHf_{100-x})_yCu_{100-y}$ alloys in liquid Mg and then impregnated by bisphenol F epoxy resin (BPF). Fig. 1 illustrates the microstructure of the interpenetrating-phase composites of Ti_xHf_{100-x} alloys and BPF (Ti_xHf_{100-x}_BPF). The polymer phase is hardly visible on the polished surface of the composites what is in agreement with [28]. The blur contrast of the metallic ligaments under the polymer layer directly indicates the presence of the polymer phase. Moreover, as a small chain-length resin, BPF has low viscosity, facilitating impregnation. As has already been shown for nanoporous gold and was confirmed by the fact that we could effectively polish the samples without destroying its internal structure, the vacuum impregnation achieves complete filling of the entire pore space with no voids [29]. The microstructures of the Ti_xHf_{100-x} scaffolds agree with the uniformly interconnected network structure (Fig. 1). The X-ray diffraction analysis indicates that the Ti_xHf_{100-x} alloys are single phase materials and consist of hexagonal close-packed phase (Fig. 2). This is in agreement with the literature, e.g. the Ti-Hf phase diagram [26,27,30].

The characteristic microstructural parameters of the Ti_xHf_{100-x} scaffolds such as mean ligament sizes, *L*, and volume fraction of metal phase, φ, are listed in Table 1. As it can be seen from the Table 1, the metal volume fraction increases from 54 ± 3 to 59 ± 2 vol% for $Ti_{75}Hf_{25}$ and $Ti_{50}Hf_{50}$ scaffolds, respectively. Samples exhibit a notable shrinkage during dealloying in a range from 3.9 to 9.8 vol% (Table 1). The shrinkage is lower for the alloys with higher Hf content. Comparing the shrinkage behavior of the current $(Ti_xHf_{100-x})_{40}Cu_{60}$ alloys and the $Ti_{40}Cu_{60}$ alloy in Mg [13], it can be concluded that Hf additions can be used for suppressing shrinkage during dealloying. The shrinkage influences solid fraction and, therefore, the mass-density of the porous scaffolds. The current porous Ti_xHf_{100-x} alloys possess low mass density values in a range from 3.9 to 5.1 g cm^{-3} (Table 1).

The porous Ti_xHf_{100-x} alloys can be classified as an ultrafine-structured material according to its fine microstructural features. The mean ligament size varies from 0.67 ± 0.11 μm to 0.79 ± 0.12 μm slightly increasing with higher Hf content. These values are notably lower compared to those reported for dealloying-based porous Ti [13]. This suggests that Hf additions are useful for the microstructural refinement of dealloying-based porous titanium. The smallest interligament spacing of about 230 ± 90 nm corresponds to the porous $Ti_{75}Hf_{25}$ with the smallest ligament size (Table 1). Larger magnification of the microstructure resolves some more notable features. The ligaments consist of rounded particles joint to each other similar to a sintering microstructure (Figs. 1b, d and f). However, the polymer phase is hardly visible on the polished surface of the composites even at higher magnifications. The complete impregnation of the composites by BPF was confirmed by analysis of mechanical behavior of the porous and composite samples and is discussed below.

The quasi-static mechanical tests of the porous and the composite materials are shown in Fig. 3a. The porous Ti_xHf_{100-x} alloys exhibit significant plastic deformability with strains of several 10% prior to failure under compressive loading. Consistent with the large plastic deformability of the porous alloys is the pronounced strain-hardening, which promotes uniform plastic flow. The large compressive strains

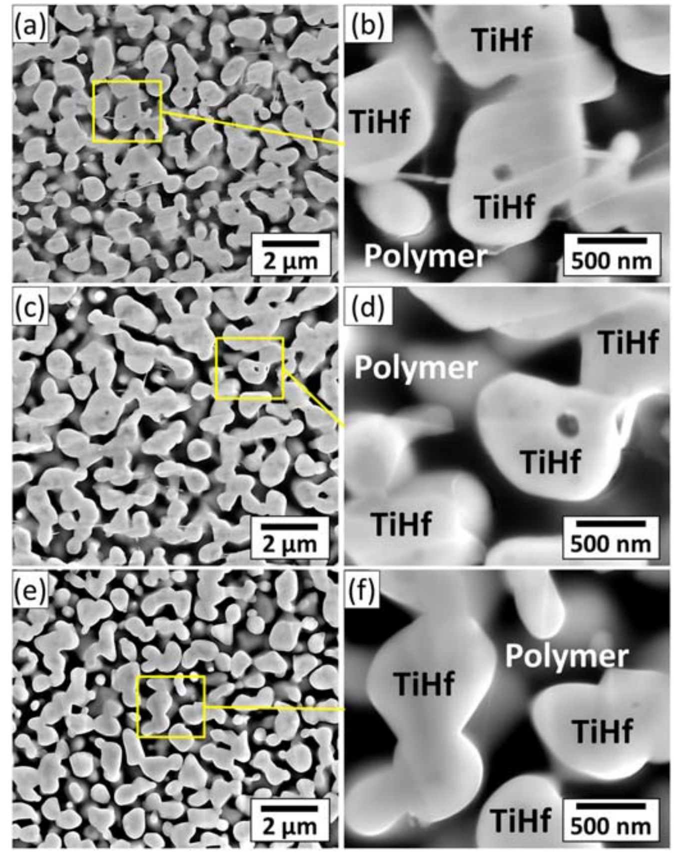

Fig. 1. Microstructure of the interpenetrating-phase Ti_xHf_{100-x}_BPF composites. (a, b) $Ti_{50}Hf_{50}$_BPF; (c, d) $Ti_{62.5}Hf_{37.5}$_BPF; and (e, f) $Ti_{75}Hf_{25}$_BPF.

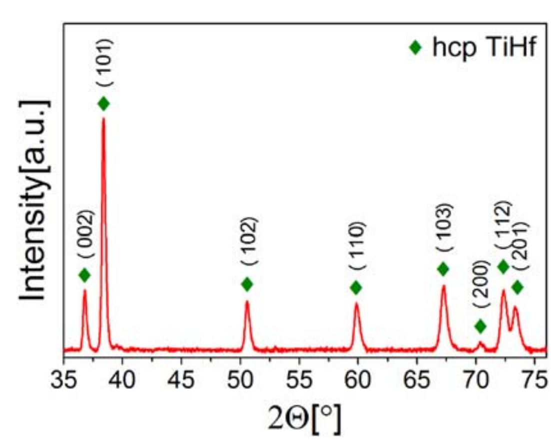

Fig. 2. X-ray diffractogram of the open porous $Ti_{50}Hf_{50}$ alloy. This is representative for the Ti_xHf_{100-x} alloys synthesized in this study.