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Elaboration of nanoporous copper by modifying surface diffusivity by the minor addition of gold

Zhenhua Dan [a,b,*], Fengxiang Qin [b], Yu Sugawara [a], Izumi Muto [a], Nobuyoshi Hara [a]

[a] *Department of Materials Science, Tohoku University, Sendai 9808579, Japan*
[b] *Institute for Materials Research, Tohoku University, Sendai 9808577, Japan*

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ABSTRACT

The basic concept of alloying was combined with modifications of the surface diffusivity through the addition of trace metals with low surface diffusivity in order to elaborate the dealloyed nanoporous metals. Nanoporous Cu with a pore size less than 10 nm was able to be elaborated. This nanoporous Cu was fabricated through dealloying from amorphous $Ti_{60}Cu_{40-x}Au_x$ ($x = 0, 1, 2$ at.%) ribbon alloys under free immersion conditions. A bicontinuous nanoporous Cu structure formed on $Ti_{60}Cu_{40}$, $Ti_{60}Cu_{39}Au_1$, and $Ti_{60}Cu_{38}Au_2$ ribbon alloys with pore sizes of 140, 19, and 9 nm, respectively, in 0.13 M HF solution. The pore size of the nanoporous Cu dealloyed from Au-added alloys was more than one order smaller than that of the Ti–Cu alloy. The pore size depended not only on the treatment solutions and treatment time but also on the alloy compositions. The uniform distribution of an Au additive on Cu in effect modified the surface diffusivity, resulting in the formation of an ultrafine nanoporous structure. The surface diffusivity was estimated to decrease from 2.49×10^{-17} to 5.88×10^{-22} $m^2 s^{-1}$ by adding 2 at.% Au to $Ti_{60}Cu_{40}$ ribbons.

1. Introduction

Nanoporous metals, as novel functional materials, have great potentials in applications as diverse as catalysis, sensors, actuators, fuel cells and microfluidic flow controllers, just to name a few [1–4]. Dealloying is a process which originated from the phenomenon of selective corrosion, and it has been attracting attention recently as an effective method to fabricate nanoporous metals with a three-dimensional (3D) bi-continuous interpenetrating pore-to-ligament structure at the nanometer scale [5–8]. Dealloying has been observed in numerous binary alloy systems including the systems: Zn–Cu [7,9], Mg–Cu [10], Al–Cu [7,11–16], Ni–Cu [7], Mn–Cu [17,18], Zr–Cu [19] and Ti–Cu [20].

The microstructure of starting materials plays an important role in the formation of the final nanoporous structure. The presence of intermetallics or second phases has been shown to facilitate the formation of a bimodal nanoporous structure from crystallized Al–Cu alloys systems [11–16]. As has been reported, nanoporous Cu was fabricated from amorphous Ti–Cu alloy systems [20] in HF solutions. It has been suggested that amorphous alloys may be better starting materials than crystalline alloys to achieve the formation of a uniform distribution of nanoporosity because of the absence of multimodal structures [20].

The sizes of the nanopores obtained from the systems mentioned above changed from a few tenths of nanometers to a few hundredths of nanometers, which was noted for the Zr–Cu system with a pore size of 500 nm [19]. The pore size had a significant effect on the mechanical properties of the nanoporous metals. The smallest nanopores that we are aware of at present is in the order of 3.5 nm for the Cu–Pt system [21]. The yield strength of nanometer-sized ligaments of nanoporous Au increased from ~880 MPa to 4.6 GPa as the pore size decreased from 50 to 10 nm [22]. Hayes [17] reported a yield strength of 128 ± 37 MPa for nanoporous Cu with a ligament diameter of 135 ± 31 nm. The yield strength of nanoporous Cu fabricated by the one-step dealloying of the melt-spun Al-50 at.% Cu alloy was determined to be 86 ± 10 MPa with ligaments of 300–500 nm [11]. The better surface enhanced Raman scattering effects and the catalysis properties of various nanoporous metals were enhanced by the finer nanoporous structures [1,18,23]. It is therefore important to fabricate nanoporous metals with ever finer nanostructures, with smaller pore sizes and ligament scales. Ultrafine nanoporous structures have been obtained at lower elevated temperatures [13,24]. Low-temperature dealloying was carried out to refine dealloyed structures with a pore size of about 5 nm due to the 3-order decrease in the surface diffusivity of Au [24]. The ligament sizes of the nanoporous Cu obtained from Al-35 at.% Cu through dealloying in a 10 wt.% NaOH solution decreased from 350 nm at 363 K to 30 nm at 298 K [13].

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* Corresponding author. Address: Department of Materials Science, Tohoku University, 6-6-02, Aza-Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan. Tel./fax: +81 22 795 7299.

E-mail addresses: zhenhuadan@material.tohoku.ac.jp (Z. Dan), fxqin@imr.tohoku.ac.jp (F. Qin), sugawaray@material.tohoku.ac.jp (Y. Sugawara), mutoi@material.tohoku.ac.jp (I. Muto), haran@material.tohoku.ac.jp (N. Hara).

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The evolution of the nanoporosity is regarded as a spinodal decomposition process occurring at the solid/electrolyte interface, and this thermally-activated process exhibits Arrhenius behaviors [13,24–26]. The evolution of nanoporosity might be affected by the composition elements in the alloy systems with different properties in surface diffusivities. The surface diffusivity of nanoporous Au is considerably lower, in fact several orders in magnitude lower than Cu [13,24,26]. The dealloying process is evoked at the metal/electrolyte interface, and the diffusivity of the more noble metal played an important role in the rearrangement of the atoms [27,28]. The surface mass-transfer diffusion coefficients of Au and Cu were reported to be 2.7×10^{-19} and 1.2×10^{-14} $m^2 s^{-1}$ at room temperature [29]. From the aspect of the difference in the surface diffusivity of the residual metals of ternary alloy systems, such as Al–Cu–Au and Ti–Cu–Au, it may well be that the involvement of the minor metals with a low surface diffusivity (Au) changes the dealloying behavior of the dominant metals (Cu). The Au addition is expected to refine the nanoporous Cu.

This paper is part of a series of efforts aimed to examine the range of the characteristic length scales of the pores and ligaments of nanoporous Cu that can be obtained through the addition of more noble metals with low surface diffusivity at room temperature. In this paper, we focus on the change in the surface diffusivity and examine the effect of the Au addition into the Ti–Cu alloy system on the formation of the nanoporous Cu structure through dealloying $Ti_{60}Cu_{40-x}Au_x$ (x = 0, 1, 2 at.%) in hydrofluoric acid solutions. The surface diffusivity of the Au-added Ti–Cu alloys was also investigated.

2. Experimental

2.1. Sample preparation

Ternary alloys with nominal compositions of $Ti_{60}Cu_{40-x}Au_x$ (x = 0, 1, 2 at.% Au) were prepared by arc melting a mixture of pure Ti (99.99 wt.%), pure Cu (99.9 wt.%) and Au (99.9 wt.%) in an Ar atmosphere. The melt spinning method was used to prepare amorphous Ti–Cu–Au ribbons 20 μm in thickness and 2 mm in width. The chemical compositions of the melt spun alloy ribbons were determined by EDX, as shown in Table 1.

2.2. Dealloying of Ti–Cu–Au samples

The dealloying was performed in hydrofluoric acid (HF) solutions in a free corrosion condition open to air at 298 K. The concentrations of the HF solution were 0.03 M (pH 3.3) and 0.13 M (pH 2.9), hereafter referred as Sol-1 and Sol-2. After 43.2 ks of immersion, the dealloyed ribbons were taken out and well rinsed with alcohol to remove any residual HF solution.

2.3. Microstructure characterization

The amorphicity of the as-spun Ti–Cu–Au samples was confirmed by X-ray diffractometer (Bruker AXS, D8 Advance) with Cu Kα radiation (λ = 1.5418 Å). The microstructures of as-prepared and as-dealloyed Ti–Cu–Au ribbons were investigated by a transmission electron microscope (JEOL, JEM-HC2100) and a high-resolution transmission electron microscope (JEOL, JEM-ARM210F). The analysis of the chemical bonding state of the as-dealloyed samples was conducted by an X-ray photoelectron spectrometer (Shimadzu Kratos, AXIS-Ultra DLD) with monochromatized Al Kα excitation ($h\gamma$ = 1486.6 eV). The morphology of the as-dealloyed samples was observed by a scanning electron microscope (JEOL, JIB-4610F). The chemical composition of the as-dealloyed samples was analyzed by an energy dispersive X-ray spectroscope (JEOL, JIB-4610F).

Table 1
Chemical composition of as-spun $Ti_{60}Cu_{39}Au_1$ and $Ti_{60}Cu_{38}Au_2$ ribbon alloys by EDX analysis.

	Content, at.%	
	$Ti_{60}Cu_{39}Au_1$	$Ti_{60}Cu_{38}Au_2$
Ti	60.1	60.1
Cu	38.9	37.9
Au	1.0	2.0

3. Results

3.1. Characterization of as-spun ribbon alloys

Fig. 1 shows the XRD patterns of as-spun $Ti_{60}Cu_{40}$, $Ti_{60}Cu_{39}Au_1$ and $Ti_{60}Cu_{38}Au_2$ ribbons. A strong broad diffraction peak around 41° and a weak broad diffraction peak at 70–75° appeared in the XRD patterns of as-spun Ti–Cu–Au ribbons, which indicated that those specimens had an amorphous structure. Fig. 2 shows the high-resolution TEM images (HRTEM) and corresponding selective area diffraction patterns (SADP) of as-spun $Ti_{60}Cu_{40}$ and $Ti_{60}Cu_{38}Au_2$ ribbons. The presence of the two halo rings, corresponding to two diffraction peaks in XRD patterns, indicates that the $Ti_{60}Cu_{40}$ and $Ti_{60}Cu_{38}Au_2$ alloys have a typical amorphous structure. The HRTEM image shows that as-spun $Ti_{60}Cu_{38}Au_2$ ribbon alloy had an amorphous structure without the crystalline clusters and phase segregations. As is well known, Au has a similar crystal structure to Cu, therefore the addition of minor amounts of Au has no significant influence on the structure of as-spun alloys. The amorphous alloys have a unique microstructure without defects existing, such as grain boundaries or alloy element segregations in chemical compositions. It is expected that the amorphous alloys are good starting materials for the formation of uniform nanoporous structures.

3.2. Characterization of as-dealloyed nanoporous structure

Fig. 3 shows the surface morphology and typical EDX spectrum of the as-dealloyed $Ti_{60}Cu_{40}$ ribbons in Sol-1 and Sol-2 after immersion of 43.2 ks. The mean pore size of the nanoporous structure of as-dealloyed $Ti_{60}Cu_{40}$ ribbons was about 71 nm after dealloying in Sol-1 and 140 nm after dealloying in Sol-2. The pore size increased with the concentration of HF solutions. After

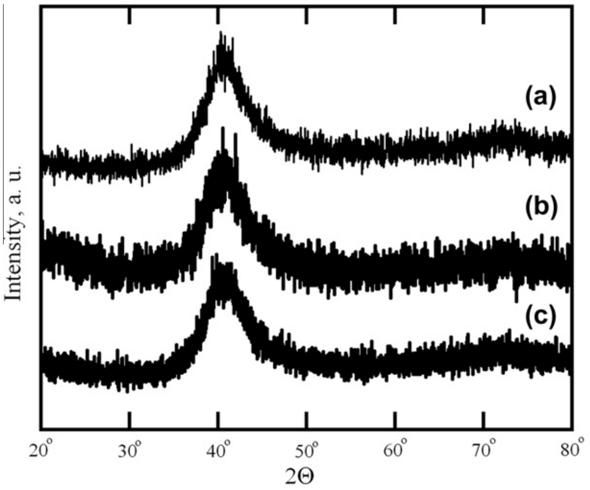

Fig. 1. XRD patterns of as-spun $Ti_{60}Cu_{40}$ (a), $Ti_{60}Cu_{39}Au_1$ (b) and $Ti_{60}Cu_{38}Au_2$ (c) ribbons.