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Short communication

Nanoporous Cu wide ribbons with good mechanical integrity

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ABSTRACT

In this work we report the fabrication of nanoporous Cu wide ribbon samples by electrochemical dealloying the minor Si alloyed γ-$Cu_{30}Mn_{70}$ solid solution alloys. The γ-$Cu_{30}Mn_{70}$ structure was found to be capable of trapping a minor amount of Si as solute by liquid quenching. Ribbon samples of 10 mm wide with tunable thickness were made at the $Cu_{28}Mn_{70}Si_2$ composition. The γ-$Cu_{28}Mn_{70}Si_2$ alloy can be turned into wide ribbon nanoporous Cu with the pore size of ~30–50 nm and with good mechanical integrity. A thin layer of Si-enriched glue structure with ~50 nm thickness was formed continuously along the grain boundaries to play the role of reinforcement for the dealloyed structure.

1. Introduction

Dealloying, during which one or several elements are preferentially dissolved from an alloy, has demonstrated a very effective strategy to turn alloys in to nanoporous (NP) metals [1,2]. NP metals made by dealloying possess a network of percolated nanopores, and the mean pore sizes are in the range from a few to several hundreds of nanometers [3,4]. The combination of nanoporosity with the properties characteristic of metallic in the materials gives rise to unusual physical and chemical properties. NP metals represent a class of ideal electrode or substrate materials for electrocatalysis [5–7]. The surface nanoporosity in some NP metals exhibit unique physical responses to visible light excitation such as the anomalous surface plasmon resonance [8] and the surface-enhanced Raman scattering (SERS) effect [9,10]. Due to these unusual optical properties, NP metals are also promising sensor materials in molecular diagnostics. The new materials are currently believed to have a wide range of potential applications in catalysis, absorption, sensing, and nanomechanics [3].

A dealloyable solid solution alloy usually consists of constituents of well-separated electrode potentials in their pure forms, and is enriched in the less noble metal. Upon dealloying, the majority less noble metals are dissolved out from the alloy. Volume contraction can occur during the process, which leads to massive cracking in the samples [11,12]. The mechanical integrity of NP metals appears to be a critical problem for their application as devices. In several recent studies, crack-free NP-Au bulk samples have been obtained by optimizing the precursor binary alloy composition and the electrochemical dealloying factors [13], or by multi-step dealloying [14]. Few such studies have been made for NP-Cu. Hayes et al. [12] reported the synthesis of monolithic NP-Cu from a low cost precursor alloy, $Cu_{30}Mn_{70}$. Chen et al. [10] have fabricated NP-Cu with tunable nanoporosity for SERS applications by dealloying $Cu_{30}Mn_{70}$ melt-spun samples of ~20 μm thick and ~1 mm wide. The presence of cracks in the samples was considerable, and hence the robustness of the NP-Cu structures was poor. In the present work, we attempt to modify the $Cu_{30}Mn_{70}$ alloy by minor alloying it with the glass-forming element Si. It is expected that a small amount of Si addition to the alloy would alter the viscosity of its under cooled liquid for the ease of wide ribbon sample preparation by liquid quenching, on the one hand, and would result in improved mechanical integrity in the wide ribbon NP-Cu samples, on the other.

2. Experimental

Alloy ingots with compositions $Cu_{30-x}Mn_{70}Si_x$ (x = 0, 0.5, 1, 2, 5) were prepared by induction melting the mixture of appropriate amount of copper (purity: 99.99 wt.%), manganese (99.5 wt.%), and silicon (99.999 wt.%) in Al_2O_3 crucibles under a vacuum level of about 5×10^{-4} Pa. Using the master alloys, ribbon samples were made by means of single-roller melt-spinning in vacuum. A HZ-3000 potentiostatic was employed to drive the dealloying in a standard three-electrode cell with a platinum counter electrode and a saturated calomel electrode reference electrode, and the

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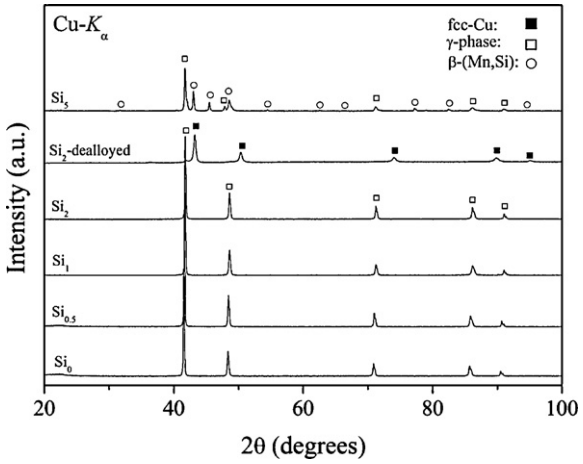

Fig. 1. X-ray diffraction patterns of $Cu_{30-x}Mn_{70}Si_x$ ($x = 0, 0.5, 1, 2, 5$) melt-spun alloys and of the as-dealloyed $Cu_{28}Mn_{70}Si_2$ sample. The subscript numbers of Si_x stand for the Si contents.

dealloying experiments were done with the dilute HCl solution freely exposed to air at 298 K. Phase identification for the melt-spun and as-dealloyed samples was conducted via standard θ–2θ X-ray scan on a Rigaku RINT-ultima IIIsp diffractometer (Cu Kα, $\lambda = 0.15406$ nm). The morphology and composition of dealloyed residues were studied using a field emission scanning electron microscope (Hitachi S-4800 SEM) equipped with an Oxford energy dispersive X-ray spectroscope (EDX).

3. Results and discussion

The X-ray diffraction patterns of the rapidly quenched $Cu_{30-x}Mn_{70}Si_x$ ($x = 0, 0.5, 1, 2, 5$) ribbon samples are shown in Fig. 1. It is seen that the FCC γ-phase structure sustains with increasing Si content up to 2 at.%, and β-(Mn,Si) phase of primitive cubic structure was precipitated as a secondary phase in the sample containing 5 at.% Si. Examination of the diffraction patterns of the single phase samples reveals a progressive shift of the diffraction peaks to higher angles with increasing Si content, which indicates that the lattice constants of γ-phase get reduced against the extended solution of Si in the alloys.

The minor alloying effect of Si on the stability of γ-$Cu_{30}Mn_{70}$ may be considered in terms of the atomic size factor and the enthalpy of mixing between constituent elements. The Goldschmidt radii of Cu and Mn are 0.128 and 0.126 nm, respectively [15]. The atomic size of Si in an alloy is dependent on its bonding states with the other elements. The ionic size of Si in the case of covalent bonding is 0.117 nm, while in a 12-coordination metallic bonding state it turns to be 0.132 nm [15]. The enthalpies of mixing between Cu, Mn and Si at 1:1 atomic ratio are $\Delta H_{Cu1Mn1} = 4$ kJ/mol, $\Delta H_{Cu1Si1} = -2$ kJ/mol, and $\Delta H_{Mn1Si1} = -28$ kJ/mol, respectively [16]. The strongly negative enthalpy of mixing between Mn and Si would suggest their strong chemical affinity in the $Cu_{30-x}Mn_{70}Si_x$ alloys. Therewith, the reduced γ-phase lattice constants are likely to be mainly attributed to the covalent bonding characteristic of Si and Mn atoms in the alloys.

The viscosity of the undercooled liquids of $Cu_{30-x}Mn_{70}Si_x$ alloys will be modified due to the change in the atomic interactions, and as a consequence the flow processing behaviors of the alloys will be altered. In the melt-spinning experiment, wide ribbon samples with tunable thickness were readily made at the $Cu_{28}Mn_{70}Si_2$ composition, while it was hardly available at $Cu_{30}Mn_{70}$. A piece of segmented ribbon sample of 10 mm wide is shown Fig. 2(a). Comparing with the traditional means for the preparation of precursor solid solution alloys [17], the realization of wide ribbon form alloys by liquid quenching ensures a time-favored and energy-saving processing technique.

The electrochemical dealloying parameters for the γ-$Cu_{28}Mn_{70}Si_2$ wide ribbon alloy was optimized via an extensive study. A driving potential range from −500 to −700 mV in 0.05 M HCl has been identified for the realization of uniform nanoporosity. The optical morphologies of the as-spun and as-dealloyed samples are presented in Fig. 2. The original shape and size of the sample are found to be preserved fairly well after the dealloying treatment. As shown by the corresponding XRD patterns (Fig. 1), after dealloying the γ-$Cu_{28}Mn_{70}Si_2$ phase has turned nearly completely into the pure copper phase. For comparison, NP-Cu samples were also made from the $Cu_{30}Mn_{70}$ ribbon samples measuring 1 mm wide and 20 μm thick under the optimal dealloying conditions given in Ref. [10]. The SEM images in Fig. 3(a) and (b) show the surface morphologies of the NP-Cu ribbons made from the two different precursor alloys, respectively. Massive cracking is evident over the entire surface of the NP-Cu ribbon made from γ-$Cu_{30}Mn_{70}$. Crack defects appear much less significant in the wide ribbon NP-Cu

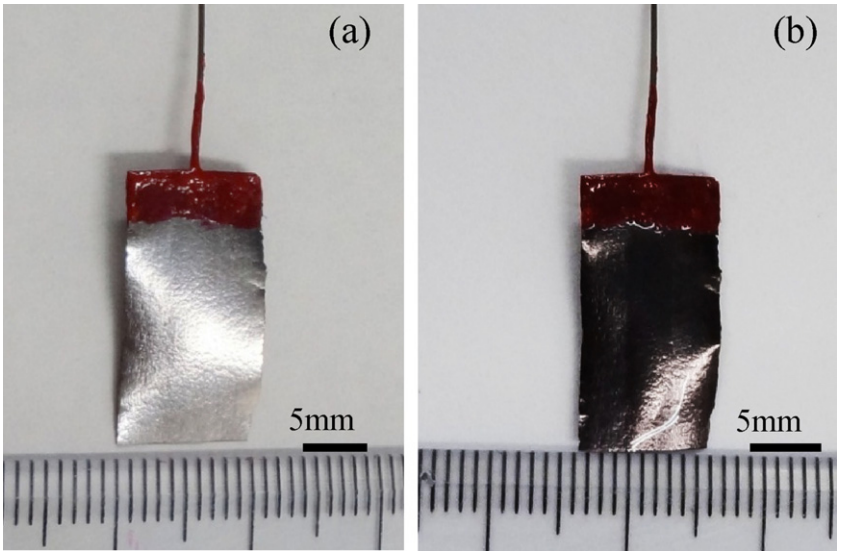

Fig. 2. Optical morphologies of (a) the as-spun and (b) as-dealloyed $Cu_{28}Mn_{70}Si_2$ wide ribbon samples.