Monolithic nanoporous copper by dealloying Mn-Cu

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Monolithic nanoporous copper was synthesized by dealloying $Mn_{0.7}Cu_{0.3}$ by two distinct methods: potentiostatically driven dealloying and free corrosion. Both the ligament size and morphology were found to be highly dependent on the dealloying methods and conditions. For example, ligaments from 16 nm–125 nm were obtained by dealloying either electrochemically or by free corrosion, respectively. Optimization of the starting Mn–Cu alloy microstructure allowed us to synthesize uniform porous structures; but we found cracking to be unavoidable. Despite the presence of unavoidable defects, the nanoporous material still exhibits higher than expected yield strength.

I. INTRODUCTION

Nanoporous metals often display novel physical, chemical, and mechanical properties due to their high surface-to-volume ratio and low densities. These properties, such as increased chemical activity and high specific strength, show promise for a variety of scientific and engineering applications, including surface-enhanced Raman spectroscopy (SERS) and catalysis.^{1–4} Furthermore, a recent study demonstrated that nanoporous gold has a high yield strength, and though the material is reported to be brittle, it presents the possibility for a high-strength material.⁵

Currently, the most promising way to create a homogeneous nanoporous structure is through the electrochemical process of dealloying.^{6,7} Dealloying occurs when an alloy is immersed in an electrolyte under a driving force such that the more reactive component dissolves, and the more noble component remains stable in metallic form. The dealloying produces a nanoporous metal with uniform and homogeneous properties throughout the dimensions of the sample.^{8–10} The driving force can be an applied potential or a suitably chosen electrolyte. The evolution of the dealloyed morphology has been examined in detail for Ag–Au alloys.^{9,11–13}

Here we show that low-density, monolithic, nanoporous copper can be synthesized by dealloying a

Mn–Cu alloy of suitable composition. Nanoporous copper has several useful attributes for studying nanoporous structures, such as low density, large modulus of elasticity, and low cost of precursor materials. Furthermore, non-monolithic nanoporous Cu in the form of Raney copper has been found to be an effective catalyst.^{14,15}

To obtain isotropic, bicontinuous, porous structures by dealloying binary alloys, the starting alloy must have complete single phase solid solubility (e.g., Ag–Au, Cu– Pt). Additionally, the oxidation potentials of the elemental metals must be different enough to allow the selective removal of one constituent. The Cu alloy that best fits these requirements is Mn–Cu.

It has been previously shown that porous structures can be created by dealloying Mn-Cu; however, no studies have been conducted on alloys with copper contents well below 50 at.%.¹⁶⁻¹⁸ Keir and Pryor¹⁶ dealloyed Mn_{0.5}Cu_{0.5} and Mn_{0.25}Cu_{0.75} alloys electrochemically in 0.5 M NaCl solutions and achieved porous structures. Another study by Min and Li¹⁷ investigated the dealloying of Incrumet (Cu, 43-51 at.% Mn and 3-5 at.% Al) in 0.3 M NaCl. They observed a strong influence of the initial alloy condition on the final pore structure. Specifically, dealloying a cold worked sample versus an annealed sample changes the pore size from 1 µm to 0.1 µm, respectively. They attributed the reduction in pore size to a reduction in phase inhomogeneities during annealing, but it may also have been due to an increase in Ostwald ripening of the ligaments driven by residual stresses in the cold rolled structure (based on a recent study that determined that elastically stressed solids have increased coarsening kinetics¹⁹).

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The formation of non-monolithic nanoporous Raney copper^{4,20–22} through a dealloying process has also been known for many years.^{14,15} Typically, Raney copper is made by dealloying small granules of Al₂Cu alloy or Al₂ZnCu alloy in NaOH.²⁰ Al-rich phases in the alloy that are completely dissolved during dealloying create a highly defected porous structure. These defects are inconsequential to the use of Raney copper as a catalyst, since the main property required is high surface area; however, they are not adequate when a homogeneous material is needed for its structural properties because uniformity and contiguity are key requirements.

These examples highlight that the starting alloy condition is of critical importance to the formation of a uniform, reproducible, monolithic porous structure. Herein, we report on the formation of monolithic nanoporous copper with pore sizes ranging from 16 nm–125 nm and a relative density of approximately 30% by dealloying $Mn_{0.7}Cu_{0.3}$. Specifically, we address the synthesis, structure, and mechanical properties of nanoporous copper.

II. EXPERIMENTAL DETAILS

The Mn–Cu phase diagram indicates that a solid solution $Mn_{0.7}Cu_{0.3}^{23}$ alloy could be made by lowering the temperature of a melt into the single phase region, holding it at that temperature to homogenize, and then rapidly quenching in water to room temperature to avoid secondary phase formation. This process yields a homogeneous, single phase Mn–Cu alloy. The standard reversible potential of Mn is –1.135 V standard hydrogen electrode (SHE), whereas Cu is 0.342 V SHE. The 1.477 V difference makes this alloy an ideal candidate for dealloying.

Mn_{0.7}Cu_{0.3} alloys were made from Cu shot (99.95%, Mallinckrodt, Phillipsburg, NJ) and Mn granules (99.95%, Alfa Aesar, Ward Hill, MA) by two techniques. In the quench furnace technique, the metals were placed in an alumina crucible suspended in a vertical tube quench furnace under flowing Ar [0.5 cubic feet per min (CFM)]. The crucible was raised into a 1300 °C hot zone, and held at temperature for 20 min, then furnace cooled to 900 °C (approximately 20 min). At this temperature, a homogeneous (Cu, γ Mn) solid solution is stable. It was held for 72 h at this temperature to anneal, then dropped through an aluminum foil seal into a water bath at room temperature. In the arc melt technique, the alloy was arc melted under vacuum on a water cooled Cu hearth, then sealed under vacuum in a quartz tube, annealed at 900 °C for 96 h, and quenched into water. The resulting ingots were sectioned, using a diamond saw, into samples approximately 300 µm thick. Metallurgical samples were polished to a 1 µm finish with diamond paste for optical microscopy and scanning electron microscopy and energy dispersive x-ray (SEM/EDX) analysis. Samples for dealloying were polished with 1200 grit SiC paper.

Dealloying was performed under free corrosion in four electrolytes: dilute HCl (pH 1.3); 1 M citric acid (pH 1.3); 1 M (NH₄)₂SO₄ + 0.01 MnSO₄ (pH 5) and 0.01 M $H_2SO_4 + 0.001 \text{ M MnSO}_4 \text{ (pH 1.9)}$. One sample was also dealloyed under potentiostatic control in 0.01 M H₂SO₄ + 0.001 M MnSO₄. All electrolytes were made with 18.3 M Ω deionized (DI) water and reagent grade chemicals. Samples were placed directly in the electrolytes for dealloying by free corrosion and left for a period of time (typically between 2 and 10 days) sufficient for complete dealloying. Dealloying time varied depending on thickness of the sample (typically between 200 and 400 μ m) and the dealloying electrolyte. A Gamry PCI4/300 potentiostat (Gamry Instruments, Warminster, PA) was used to drive the electrochemical dealloying with a platinum cathode and a saturated mercury sulfate reference electrode. After dealloying, the sample was removed from the electrolyte and placed in pure DI water to displace the electrolyte from the internal pores. The sample was then allowed to air dry.

Optical microscopy was performed with a differential interference contrast microscope, and electron microscopy was performed with a field emission scanning electron microscope equipped with energy dispersive x-ray spectroscopy (EDX). The mechanical properties of nanoporous Cu were tested by depth-sensing nanoindentation using a Hysitron Triboindenter with a Berkovich tip (tip radius of ~200 nm). A total of 75 indents (5 × 5 grids on three different sections of the sample) were performed on a single-point diamond turned surface (rms roughness ~100 nm), using a constant loading rate of 500 μ N/s with loads ranging from 500–2000 μ N. The indent depths ranged from 350–810 nm.

III. RESULTS AND DISCUSSION

A. Metallurgy

Both methods of creating the $Mn_{0.7}Cu_{0.3}$ alloy yielded single phase areas, with regions near the top and edges of the ingots containing multiple phases. Figure 1 shows a differential interference contrast optical microscopy image of a single phase region from a quench furnace technique sample. Inclusions can be seen in the alloy. They were examined by EDX and determined to consist primarily of manganese oxide and sulfide precipitates. In general, we observed that the arc melted alloy had considerably more inclusions (~1700 cm⁻²) than the furnace melted alloy (~200 cm⁻²). Depending on the dealloying chemistry and conditions, these inclusions can either remain in the structure or be removed, forming voids.

B. Dealloying

Alloy samples were placed in the electrolytes under free corrosion for a period of between 2 and 10 days, depending on sample size and electrolyte. Hydrogen



FIG. 1. Optical micrograph of the $Mn_{0.7}Cu_{0.3}$ alloy formed by melting under flowing argon in a tube furnace, with subsequent annealing at 900 °C for 72 h and water quenching. Manganese oxide and sulfide inclusions formed with a density of ~200 cm⁻².

bubbles formed on the surface of the alloy during dealloying consistent with the extremely low reversible potential of Mn. The completion of dealloying is indicated by the cessation of hydrogen evolution. Dealloying produced monolithic nanoporous Cu with a relative density $(\rho_{sample}/\rho_{Cu})$ of $30 \pm 2\%$, as determined by the mass and volume of the dealloyed samples, consistent with the alloy composition. The porous Cu samples were mechanically robust, yet had to be carefully handled due to the brittle nature of the material.

Dealloying in different electrolytes leads to significantly different ligament morphologies and length scales, yet all of the electrolytes still generated bicontinuous ligament structures. Figures 2(a)-2(d) show fieldemission scanning electron microscopy (FESEM) images of the furnace melted alloy dealloyed in four different electrolytes: (i) pH 1.3 HCl, (ii) 1 M citric acid, (iii) 0.01 $M H_2SO_4 + 0.001 M MnSO_4$, and (iv) $1 M (NH_4)_2SO_4 +$ 0.01 M MnSO₄. The structure formed by pH 1.3 HCl exhibits a smooth ligament morphology, with an average ligament diameter of 125 ± 30 nm and residual Mn content of 0.2 at.% by EDX after 8 days free corrosion. Dealloying under free corrosion in citric acid results in ligaments with diameters of 80 ± 20 nm, which are not as smooth or uniform as those formed by the HCl electrolyte. This sample was not completely dealloyed, even after 10 days, with 2.4 at.% Mn by EDX remaining. The solution 0.01 M H₂SO₄ + 0.001 M MnSO₄ also formed very smooth ligaments with an average diameter of $45 \pm$ 11 nm and a residual Mn content of 1.6 at.% after 6 days of free corrosion. Dealloying in ammonium sulfate resulted in ligaments with an average diameter of 53 ± 8 nm. By EDX, 4.4 at.% Mn remained after 6 days of free corrosion dealloying.

We attribute the large difference in ligament size and structure observed to the different dealloying rates and surface mobilities of Cu in the different electrolytes. Varying the electrolyte has been shown to influence the ligament structure in dealloyed Ag–Au.²⁴ It has also been



FIG. 2. Dealloying electrolytes affect both the ligament size and morphology. These SEM micrographs show the structure resulting from dealloying $Mn_{0.7}Cu_{0.3}$ in (a) pH 1.3 HCl, (b) 1 M citric acid, (c) 0.01 M H₂SO₄ + 0.001 M MnSO₄, and (d) 1 M (NH₄)₂SO₄ + 0.01 M MnSO₄.

shown in the Ag–Au system that coarsening occurs as the sample ages in the electrolyte at ambient temperature.²⁵ The effects of dealloying rate and time were seen by dealloying Mn_{0.7}Cu_{0.3} by two methods: free corrosion and under potentiostatic control. One sample was dealloyed under free corrosion in 0.01 M $H_2SO_4 + 0.001$ M MnSO₄ for 6 days, forming a smooth ligament structure with an average ligament diameter of 45 ± 11 nm. A second sample was potentiostatically dealloyed in the same solution at -0.11 V [versus mercury sulfate electrode (MSE)] for 14 h. The ligament structure is the same, but the dimensions are smaller by a factor of 3, with an average ligament diameter of 16 ± 4 nm. The use of a potentiostat significantly increased the dealloying rate, thus decreasing the total dealloying time. Previous research has shown that dealloying time affects the final ligament structure.25

C. Cracking

The presence of cracks was the most significant structural defect seen when dealloying $Mn_{0.7}Cu_{0.3}$. The cracks have a negative impact on the mechanical properties and robustness of the dealloyed structure. A sample cut from the quench furnace melted ingot was dealloyed for approximately 96 h in dilute HCl (pH 1.3), cleaved, and then viewed in cross-section with a FESEM, as seen in Fig. 3.

Some insight on the origin of the cracks can be gained by examining the crack structures. Three crack surface morphologies occur in the cleaved sample. The first type of morphology (not shown) reveals that portions of the cleaved surface are relatively non-porous, and on closer examination, are found to be covered with an enriched Cu layer. The fracture morphology of these regions suggests that the dense layers form at grain boundaries. This is confirmed by Keir and Pryor,¹⁶ who observed intergranular separation while dealloying Mn-Cu alloys at the original alloy grains, and proposed that it was due to the removal of manganese-rich grain boundaries. If the Mn concentration is increased at grain boundaries, cracks will form as the Mn is etched away, with a simultaneous formation of an enriched copper layer.¹⁷

The two other crack morphologies observed could either be caused by cracks propagating into the structure during the dealloying process, or by post-dealloying fracturing. These crack surface structures are seen in Fig. 3(a). Crack surfaces with ligaments that form a smooth, bicontinuous structure across the surface [Fig. 3(b)] are most likely formed during the dealloying process. Areas with individual fractured ligaments that terminate at the surface [Fig. 3(c)] are likely post-dealloying fractures in the monolith, which cause the individual ligaments to be severed. If these surfaces formed during dealloying, the tips of the fractured ligaments would become smooth due to coarsening.

Internal cracking in the monolith could be caused by several mechanisms: residual stress, capillary forces leading to "mud-cracking", or coherency stresses between the alloy and the dealloyed copper. First, surface cracking may be due to residual stresses formed at the surface from the mechanical cutting and polishing processes. As dealloying progresses, these stresses could relax by forming cracks at the surface. A tensile stress induced in the surface by cutting may also contribute to a stress-corrosion cracking mechanism, which may explain the presence of subsurface cracks.

Second, capillary forces during drying may generate enough stress to cause the porous copper to crack.²⁶ However, samples that were dried in a carefully controlled



FIG. 3. Quench furnace technique $Mn_{0.7}Cu_{0.3}$ sample dealloyed in pH 1.3 HCl under free corrosion for 96 h: (a) two crack surface morphologies are seen, (b) smooth bicontinuous ligament structures, and (c) rough fracture terminated ligament structures. The smooth surfaces form during dealloying, while the fracture terminated structures are caused by post-dealloying fracturing.

method to reduce capillary forces by displacing the rinse water with methanol and then allowing the methanol to evaporate at room temperature still contained these networks of cracks.

Third, cracking may form during the dealloying process due to coherency stresses at the Cu-Mn_{0.7}Cu_{0.3} interface. Mn–Cu will form a (Cu, γ -Mn) solid solution with a face centered cubic structure up to approximately 84 at.% Mn, at which point the structure becomes face centered tetragonal.²⁷ As the Mn content increases, the clattice dimension increases. The lattice parameter of $Mn_{0.7}Cu_{0.3}$ is 3.75 Å, but as dealloying proceeds, the structure changes to pure copper, with a lattice constant of 3.61 Å, which creates a lattice mismatch of 3.7%. This will create a tensile coherency stress on the ligaments between the Mn-Cu alloy and the dealloyed Cu ligaments. This stress must be accommodated by the ligaments, since the alloy is constrained by the bulk. The stress may be more readily relieved by the introduction of fractures rather than dislocations, since dislocation nucleation and movement is severely restricted by the small dimensions of the ligaments.^{28,29} The stress may also influence the behavior of the martensitic transformation,³⁰ inducing further stresses in the structure. It should be noted that the inclusions or inclusion voids left in the porous structure can serve as stress concentrators, which may lead to cracking. However, we could find no instances of cracks initiating at these sites.

D. Mechanical properties

Mechanical properties were evaluated by nanoindentation on one sample from the quench furnace technique. The sample was dealloyed for 8 days in pH 1.3 HCl under free corrosion, and had a ligament diameter of 135 \pm 31 nm. The nanoporous copper had a hardness of 128 \pm 37 MPa. It has been demonstrated that for foams with densities less than 30%, the yield strength correlates with hardness.³¹ Assuming this relationship is still valid at this scale, we can use a direct indentation as an indirect measure of the yield strength. Fully annealed polycrystalline copper has a yield strength of 55 MPa,³² which is considerably less than the measured hardness of the dealloyed copper. We attribute the high hardness to the small length scale of the ligaments, which inhibit dislocation mediated plasticity.²⁹

IV. CONCLUSION

Uniform monolithic structures of nanoporous copper can be created by dealloying Mn–Cu alloys. The alloy processing technique is critical in obtaining a homogeneous porous structure: oxide inclusions and second phases negatively affect the uniformity of the dealloyed structure. The ligament size and morphology can be controlled by the dealloying conditions, such as the choice of the dealloying electrolyte and the driving conditions of either free corrosion or potentiostatic control. Porous copper with ligaments as small as 16 nm can be obtained when dealloyed potentiostatically in H_2SO_4 , and as large as 125 nm when dealloyed under free corrosion in acid chloride. The main defects in the dealloyed structures are cracks, which form due to the removal of Mn from grain boundaries, coherency stresses caused by the lattice mismatch between the Cu ligaments and the Mn-Cu alloy, and possibly capillary stresses during drying or residual surface stresses. However, the nanoporous copper still exhibits a larger yield strength than that of annealed polycrystalline copper. Thus, low density, high surface area, high strength porous Cu creates many engineering opportunities.

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