

Science and Technology of Nanoporous Metal Films

NSF NIRT Grant 0507023

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The aim of this project is the development of a comprehensive scientific understanding of the properties and synthesis technology of nanoporous metal alloy films. The technologies for creating these films, and the properties of the resultant films, depend strongly on nanometer scale phenomena. A number of the methods, tools, and models developed to synthesize, characterize, and understand these films will be broadly applicable to other nanoscale phenomena and materials, such as nanoscale transport processes and bulk nanoporous materials. This research will investigate in detail nanoporous alloys, building on the present understanding of the dealloying process arising from corrosion investigations and synthesis of nanoporous, elemental Au films.

During the past year, we investigated two methods for synthesis of representative nanoporous metal films. These materials have been incorporated into a process sequence which makes possible the fabrication of freestanding nanoporous microstructures such as clamped bridges and membranes for the first time. These microstructures, in turn, facilitate the use of powerful tools and techniques for investigating the material properties controlled by nanoscale phenomena. For example, we have used nanoindentation tools to investigate the thermo-mechanical behavior of nanoporous Au films. Our experimental results are being fed back into theoretical and computational modeling of the synthesis process in order to understand nanoporous alloy formation at the atomic level. In this way, a three-dimensional model is being developed to simulate the selective dissolution of metal alloys.

SYNTHESIS OF NANOPOROUS METAL FILMS

Multiple-metal precursor alloy films have been synthesized in two ways: co-sputtering and electrodeposition. In the co-sputtering processing, a more noble material target and a less noble material target are sputtered concurrently by argon ions. Uniform amorphous thin film alloys are deposited on a substrate, usually single crystal silicon. Alternatively, electroplating of multielement thin films (for example, Au-Ni) results in a homogeneous solid solution, either amorphous or polycrystalline. These films are in a metastable state.

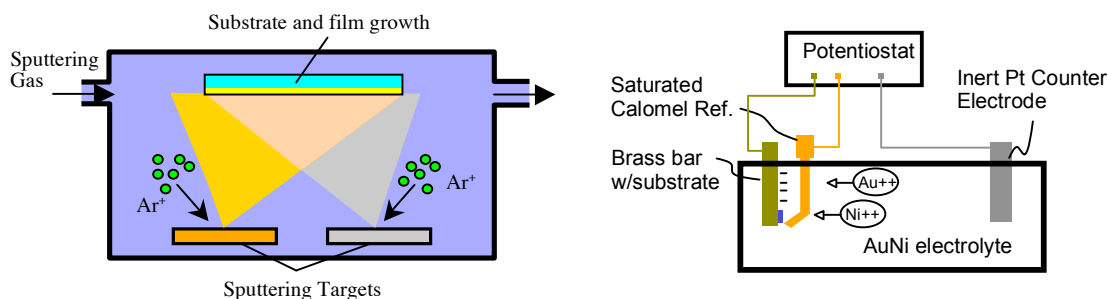


Figure 1. Multielement precursor alloy preparation (a) Co-sputtering, (b) Electrodeposition

Nanoporous metal thin films are created by dealloying the precursor alloys via chemical or electrochemical methods. These nanoporous materials exhibit a variety of morphologies, mechanical properties, and adhesion abilities (Figure 2). For electrodeposited films, the average pore size and microstructure of the dealloyed materials is found to depend on the composition and degree of crystallization of the starting film. Results show that as the Ni content increases, a coarser pore structure is obtained (Figure 3). For sputtered films, the pore size has been demonstrated to be tunable by post-dealloy thermal annealing.

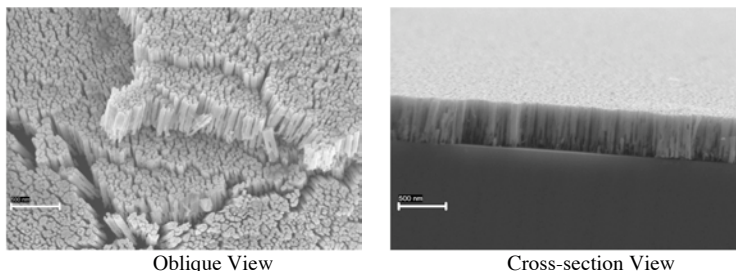


Figure 2. Nanoporous nitinol after chemical etching of aluminum from NiTi-Al.

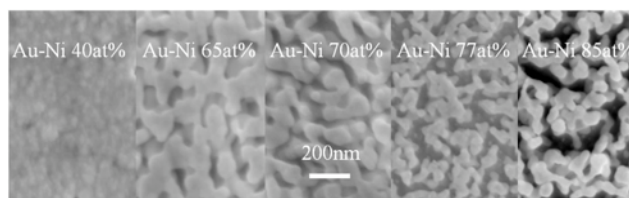


Figure 3. Dealloying of metastable Au-Ni provides a tunable microstructure. These nanoporous Au films were obtained by immersing each Au-Ni alloy in 10 mM H₂SO₄ and subsequently dealloyed under anodic potential control.

THERMO-MECHANICAL CHARACTERIZATION OF NANOPOROUS MICROSTRUCTURES

We have recently developed a method to fabricate freestanding microstructures of nanoporous Au (np-Au) by dealloying an Au-Ag alloy film patterned over a sacrificial Al layer.¹ Thermal treatments of released microstructures prior to dealloying generate sufficient compressive stress to induce plastic buckling. This buckling compensates the tensile stresses generated during the dealloying process, thus mitigating fracture of the np-Au that otherwise occurs.

Using these freestanding nanoporous microstructures, we studied the effects of thermal treatment on porosity evolution. As shown in Figure 5, different np-Au structures display various porosity evolution depending on the geometric configuration of their mechanical constraints.

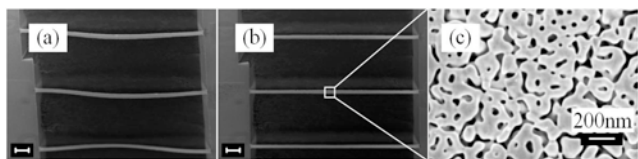


Figure 4. Comparison of plastic thermal buckling in Au-Ag bridges and np-Au bridges after dealloying. (a) SEM image (59° tilt) of Au-Ag bridges after rapid thermal annealing at 400°C. (b) SEM (59° tilt) of the same bridges after 10 minutes dealloying in concentrated nitric acid. (c) SEM showing the nanoporous morphology of the np-Au bridge. [The scale bars in (a) and (b) are 30 μm long.]¹

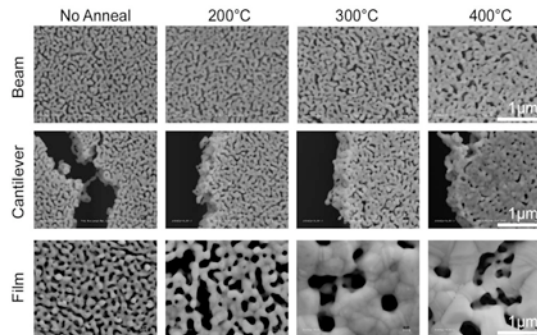


Figure 5. Effects of thermal treatment on porosity evolution of various nanoporous microstructures.^{2,3}

COMPUTATIONAL MODELING OF THE DEALLOY PROCESS

Recent results from the literature^{4,5} describe models of dealloying in which both the dissolution rate of the less noble alloy component and the surface diffusion rates of both components depend only on the coordination number of the surface atomic bonds. Initially, the rates of diffusion and dissolution were arrived at empirically – as “best fit” parameters in comparison with experimental data.

In our work, we are extending this dealloying model in two ways. First, the role of the electrolyte composition is explicitly considered, including the restricted transport in the nanopores. In addition, first-principles calculations are evaluating the metal/solution interface electronic structure and are used to probe the energetics of diffusion and dissolution processes occurring at a constant electrochemical potential. These methods will produce estimates of the diffusion and dissolution energies which can then be compared with experimental results. Finally, we are developing a three-dimensional kinetic Monte-Carlo model for simulating the selective dissolution of binary metal alloys, as shown in Figure 6.

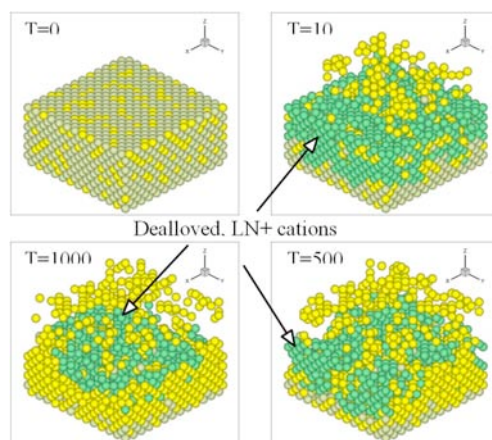


Figure 6 Model prediction of evolution of dealloying processing

NEAR-TERM MILESTONES

- Synthesis of nanoporous alloy films and investigations of the microstructure of dealloyed ternary precursor alloys;
- Investigation of nanoporous metal-semiconductor and nanoporous metal-metal heterogeneous materials with enhanced adhesion;
- Modeling and simulation of dealloying of ternary precursor alloys;
- Investigations of stress generation and mitigation mechanisms during dealloying;
- Investigations of mass transport through np-metal structures;
- Exploration of chemical sensing and catalysis applications of freestanding np-Au microstructures.

References

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