Mechanical Properties of Hierarchical Nanoporous Metal

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Abstract:

There is a lot of research focused on the fabrication of hierarchical nanoporous structures applicable to new devices. Also, polymer has attracted attention in the application of materials. Previous reports in the literature describe the synthesis protocols of nanoporous gold (NPG) obtained by dealloying Au/Ag foil with HNO_3, and nanoporous copper fabricated by Cu/Si foam dealloying using HF [1]. Furthermore, it is well known that self-organized wrinkle structures are deformable anisotropic microstructures. Those wrinkle structures can be obtained by taking advantage of the difference in Young's modulus between soft and hard materials [2]. In this report, we show the preparation and measurement surface properties of a heterostructures obtained by combining metal foam and polymer. The basic surface properties of the samples will be discussed.

Introduction:

The properties of metals and polymers are quite distinct. In this project, we focused on creating heterostructures by combining polymer and metal foam structures so as to establish a new system with applications as a sensor or actuator. Metal foams can span several length scales. In this system, the porosity is in the nanometer range that offers high surface to volume ratio and allows synthesis of porous metals with unique physical properties. This structure can be obtained via a two-step process involving synthesis of a metal alloy and its controlled corrosion (dealloying) in a solution. During dealloying one element of the alloy dissolves and the remnants self-assemble into a three dimensional sponge. The elastomer used in this project is polydimethylsiloxane (PDMS). This polymer is a soft material and any curling is easy to control via Young's modulus.

One inspiration for the project involves biomimetics that is observing and replicating functional biological surfaces and replicating their functional surfaces so as to obtain superior functional materials. For example, one of the most famous biological functions is the Lotus effect. Lotus leaf surfaces have hierarchical structures ranging from nanometer to micrometer. In previous research, we fabricated a structure that mimicked shark skin by using self-organization with a sample surface made of polymer. But shark skin surface is known to have a functional drag reduction because of its riblet structure. Our intention is to fabricate the same surface with a more durable material like metal.

Periodic buckling structures, similar to the shark skin riblet, are formed by self-organization. This "wrinkle" structure formation depends on the difference in any two material's Young's modulus. Also, the period of wrinkles depends on the hard material's height — $\Lambda \propto 2\pi h(Ef/3Es)1/3$ — where Λ is the period of wrinkle, h is the thickness of hard layer, Ef equals the hard layer's Young's modulus, and Es is the hard layer's Young's modulus.

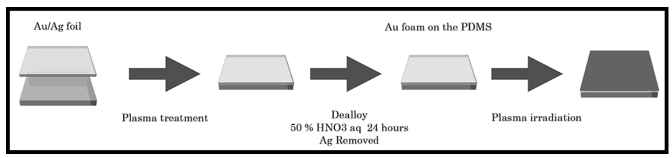

Figure 1: Gold foam on polymer process.

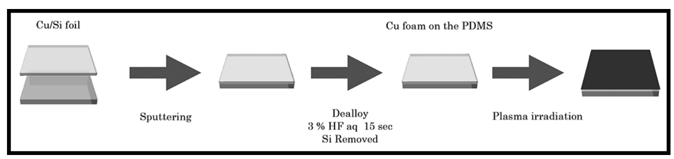

Figure 2: Copper foam on polymer process.

Experimental Procedure:

We fabricated two types of metal samples.

Gold Foam on Polymer (see Figure 1). First, we cured PDMS at 70°C for five hours. This PDMS has a Young's modulus of 1.3 MPa. We treated the PDMS surface with a plasma irradiation for 10 min, and then fixed gold (Au) and silver (Ag) complex foil (gold leaf) on top of the PDMS. NP Au foil was formed by dealloying a Au/Ag foil by using a 50% nitric acid water solution for 4, 12, and 24 hours. As a result, we obtained nanoporous gold (NPG) and polymer heterostructures. Finally, we tried using plasma irradiation to change the surface chemistry.

Copper Foam on the Polymer (see Figure 2). In the meantime, we fabricated the same structure using a different

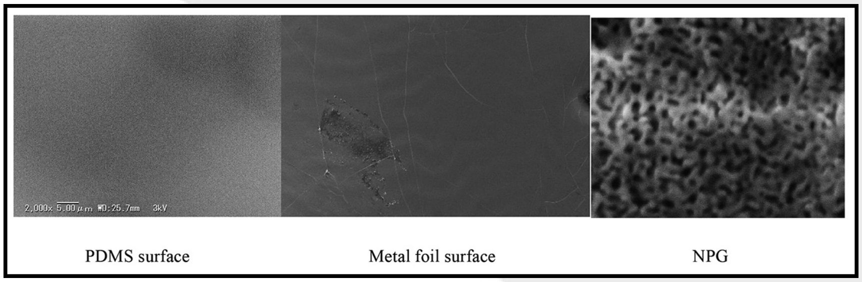

Figure 3: SEM images of surface observations.

Water contact angle

Metal : Hydrophobic
Polymer : Hydrophilic

N = 3
Average

			NPG		
	PDMS	Self standing Foil	48 Hours		4 Hours
No plasma	103.4	$\theta < 40°$	98		92.4
Plasma 10 min		N/A	Gradually Changed		
Plasma 30 min	82.5	N/A	113		98.6

Table 1: NPG contact angles.

metal. We again cured the PDMS using the same curling condition of 2-1. After that, the PDMS surface was treated by plasma irradiation for 10 min. We then obtained copper (Cu) and silicon (Si) complex layers by sputtering, and dealloyed a Cu/Si foil using 3% HF water solution for 15 sec. After that, we obtained a nanoporous Cu and polymer heterostructure. Finally, we tried using plasma irradiation for 30 min to change the surface chemistry.

Results and Discussion:

Dealloying. Dealloying NPG for 24 hours resulted in a nanoporous structure with a pore diameter around 20 nm. According to the results of a XPS survey, NPG dealloyed by NHO_3 for 24 hours had a surface that was less than 1% Ag. However after dealloying for only four hours, the sample had 6% Ag. We concluded that this porous diameter and the Au/Ag ratio depends on dealloying time. (See Figure 3.)

Wettability. A lot of biomimetic research focuses on surface wettability. In this report we show NPG contact angle measurement data in Table 1. In general, the polymer surface showed a hydrophilic surface and the metal showed a hydrophobic surface. With no plasma treatment, the polymer surface had hydrophobicity. In contrast, after plasma irradiation, the polymer surface was hydrophilic. On the other hand, our metal form results were the reverse. Also, 24 hours of dealloying the metal foam surface showed that the contact angle was more increased than a four-hour dealloying. Surface wettability depends on surface pore diameter and chemical metamorphic. We concluded that we could successfully make a hydrophilic metal porous surface.

Conclusions and Future Plans:

We obtained gold foam on PDMS, and we could see the difference in contact angles with this heterostructured surface. Also, we successfully obtained a nanoporous metal structure important for biomimetics. For future work, this structure has to make a clear buckling structure proven using the buckling equation, so we will need to change the thickness of the metal foam in order to obtain the periodic wrinkle structure. We can then consider sliding angle and reduction measurements. Such measurements can establish the combined properties of a complex heterostructure.

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