NANOFOAMS

Dealloying

Acids have been used for centuries in the purification of metals. For example, Aqua regia—a mixture of hydrochloric and nitric acid (HCl and HNO_3, respectively)—has been used for centuries to purify gold by first dissolving and then reprecipitating it.

A bit of history on Aqua Regia from Wikipedia:

When Germany invaded Denmark in World War II, Hungarian chemist George de Hevesy dissolved the gold Nobel Prizes of German physicists Max von Laue (1914, x-ray diffraction from crystals) and James Franck (1925, verification of the Bohr model of the atom) in *aqua regia* to prevent the Nazis from confiscating them. The German government had prohibited Germans from accepting or keeping any Nobel Prize after jailed peace activist Carl von Ossietzky had received the Nobel Peace Prize in 1935. De Hevesy placed the resulting solution on a shelf in his laboratory at the Niels Bohr Institute. It was subsequently ignored by the Nazis who thought the jar—one of perhaps hundreds on the shelving—contained common chemicals. After the war, de Hevesy returned to find the solution undisturbed and precipitated the gold out of the acid. The gold was returned to the Royal Swedish Academy of Sciences and the Nobel Foundation. They re-cast the medals and again presented them to Laue and Franck.

Acids dissolve different metals at different rates: "less noble" metals are dissolved faster than "more noble" metals, e.g. Ag dissolves faster in *aqua regia* than Au. This

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behavior is exploited in a separations process called "selective leaching" or "dealloying."

Start with gold leaf: a Ag-Au solid solution (Ag and Au are fully miscible). If the gold leaf is submerged in an acidic solution, the Ag is eventually dissolved away while the Au remains. The leftover Au has the morphology of a high density, on open cell foam!

The ligaments in this Au foam are very short—on the level of a few tens of nanometers—and have a low aspect ratio (i.e. their thickness is comparable to their length). Thus, dealloyed Au is sometimes referred to as "nanoporous" or as a "nanofoam." Nanofoams of metals other than Au can also be made by dealloying, e.g. Cu, Ni, and Pt.

Surface-to volume ratio

Because of their small ligament sizes, nanofoams have high surface area per unit volume. This property makes them promising for a variety of applications requiring high surface area, e.g. catalysis, sensing, filtration...

Size effect in mechanical properties

The strength of nanofoams sizes follows the Gibson-Ashby scaling relation:

$$\frac{\sigma_{pl}^*}{\sigma_{ys}} = C \left(\frac{\rho^*}{\rho_s} \right)^{3/2}$$

However, this relationship is a phenomenological—rather than mechanistic—observation: it does not imply that deformation in such foams is localized into plastic "hinges" at the nodes where several ligaments meet.

Nanofoams are stronger than would be predicted based from the properties of bulk Au because their ligaments have higher yield stress than bulk Au. This increase in strength is a "size effect": a change in mechanical properties due to the size of the sample being deformed. Three mechanisms that can lead to size effects are:

- Reduction in size of dislocation sources: decreasing ligament size increases flow stress because the maximum dislocation source size is limited by the ligament size. The stress required to generate new dislocations from short sources is higher than that required to generate dislocations from long sources.
- Dislocation starvation: increases flow stress by removing dislocations to free surfaces. For any subsequent deformation to occur, dislocation must first be renucleated from the surface, which generally requires much higher stresses than propagation of pre-existing dislocations.
- Surface tension gives rise to surface energy-induced stresses. The effect of surface tension increases with decreasing ligament size. Surface tension can alter the flow stress of nanofoams by pre-stressing the ligaments.

The effect of electrochemistry

Electrochemistry influences the surface tension of nanofoams, which in turn changes the strain in the ligaments. Based on this effect, potential applications of nanofoams in environmentally-induced actuation are also being explored (H. J. Jin and J. Weissmüller, Adv. Eng. Mater. **12**, 714 [2010]).

It has also been found that the mechanical properties of nanofoams can be reversibly tuned by electrochemistry (H. J. Jin and J. Weissmüller, Science **332**, 1179 [2011]).

Coarsening of nanofoams

Nanofoams can reduce their surface energy by coarsening, i.e. reducing their surface area per unit volume by increasing their ligament size. Surface diffusion is the most commonly proposed mechanism to explain coarsening of nanofoams

However, some aspect of nanofoam coarsening are not easily explained by surface diffusion:

- Nanofoam volume decreases upon coarsening, but surface diffusion assumes a constant number of lattice sites and therefore no change in volume
- Small voids completely enclosed in ligaments are commonly observed in nanofoams, but it is not clear how surface diffusion can lead to the formation of such voids

Network restructuring through local plastic deformation of ligaments is a coarsening mechanism that addresses the deficiencies of the surface diffusion model. It occurs spontaneously below a critical ligament size and leads to the formation of enclosed voids (K. Kolluri and M. J. Demkowicz, Acta Mater. **59**, 7645 [2011]).

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