Conference Abstracts

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Ancillary Challenges in Dealloying

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Much of the work associated with dealloying over the past few decades has been elucidation of processing conditions to make nanoporosity. Models for porosity evolution, either by electrochemical or liquid metal dealloying, are working well to understand the evolution of such microstructures, at least at the sub-grain level. Unfortunately, the utility of dealloyed materials are often limited by ancillary considerations, such as the material falls apart at grain boundaries, or is inhomogeneous either structurally or compositionally. The "zipped" grain boundaries of nanoporous gold processed from cold-rolled and annealed materials are very convenient for that material, but are not universally observed. In this presentation, I will discuss some of the general strategies we have been exploring to mitigate effects such as grain boundary separation and secondary coarsening of materials behind the dissolution front that lead to gradients in porosity. Primarily, these methods are based on careful design of the precursor alloys, but also involve careful control of the dealloying driving forces in the dealloying medium.

Trends in Pattern Formation During Dealloying in Different Solvent Media

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Dealloying has been leveraged over the past 20 years as a novel technique to fabricate bulk, self-organized nanostructures. During dealloying, one or more components are selectively dissolved while the remaining components reorganize into porous networks. Originally, dealloying was considered in an electrochemical context, but recent work has extended the concept to other solvents such as liquid metals, solid metals, and vapor. In this talk, I will discuss how the solvent impacts the rate-limiting behavior during dealloying. I will identify the key kinetic parameters controlling pattern formation and discuss how they may be tuned to fabricate materials with a variety of morphologies – globular, lamellar, and bicontinuous – and a large breadth of microstructural length scales – 30 nm to 10 μm. I will then give an overview of the promising thermo-mechanical properties of these new materials, including high thermal stability, high strength, and the potential to work harden. These results highlight opportunities for designing and synthesizing bulk nanocomposite metals with superior properties by tuning their microstructure morphology.

Nanoporous Gold - from Advanced Characterization to Future Applications

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A few years ago, we discovered that it was possible to fill nanoporous gold completely by simple electrodeposition of copper [1]. This enabled atom-probe tomography (APT) analyses that gave both expected and unexpected results. An expected result – yes, each ligament has a core-shell structure with surface enrichment of gold. But we were the first to show that in a ligament as narrow as 6 nm, the composition in the core was almost perfect original alloy. This is consistent with some atomistic simulation results. We also showed that there was always Au on the ligament surfaces when exam-ined at the highest resolution of APT, contradicting any impression that Ag might be in contact with the electrolyte in mature dealloyed layers. Later, we examined dealloyed layers formed on ternary AgAuPt alloys [2,3]. The presence of Pt greatly refines the porosity and improves the thermal stability of the nanoporous material. The exact way in which Pt enriches on the ligament surfaces is still under investigation, but essentially it forms small patches. Whilst the initial Pt enrichment may be along step edges, by the time a dealloyed layer is a few hundreds of nm thick, the Pt is mostly in these patches with only a few arguable linear features. Then, in unpublished APT work, we have examined the effect of heating the dealloyed materials in oxidizing and reducing atmospheres. Heating in air enriches Pt further on the ligament surfaces, because Pt and O have an attractive interaction, and the length scale of the porosity is quite stable. Heating in vacuum or hydrogen desegregates Pt and al-lows rampant coarsening of the nanoporous structure. But even though there is little coarsening in air, the core-shell structure is destroyed to some extent. The electrocatalytic activity of all these products has been investigated.

In parallel with the APT studies, environmental TEM studies have been carried out, using a heating stage with various atmospheres [4]. The resulting video output reveals the dynamics of the morphol-ogy evolution in the nanoporous material, with or without alloyed Pt.

1. A.A. El-Zoka, B. Langelier, G.A. Botton and R.C. Newman, Enhanced analysis of nanoporous gold by atom probe tomography, Mater. Charact., 128, 269–277 (2017).
2. A.A. El-Zoka, B. Langelier, A. Korinek, G.A. Botton and R.C. Newman, Nanoscale mechanism of the stabilization of nanoporous gold by alloyed platinum, Nanoscale, 10, 4904–4912 (2018).
3. A.A. El-Zoka, B. Langelier, A. Korinek, G.A. Botton and R.C. Newman, Advances in nanoscale characterization of refined nanoporous gold, Electrochim. Acta, 283, 611-618 (2018).
4. A.A. El-Zoka, J. Howe, R.C. Newman and D.D. Perovic, In situ STEM/SEM study of the coarsening of nanoporous gold, Acta Materialia, 162, 67-77 (2019).

Coarsening of Nanoporous Metals: Self-Similarity and Stability

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Bicontinuous two-phase mixtures are found in systems ranging from block copolymers to phase separated alloys and nanoporous metals. It is well known that during coarsening for a sufficiently long time the morphology, topology, and two-point spatial correlations of interfacial curvature found following spinodal decomposition by bulk diffusion are unique and time independent under the scaling of a characteristic time-dependent length scale, such as the inverse of the interfacial area per volume [1]. In addition, the bicontinuous structure is maintained to volume fractions as low as 36% solid [2]. Recent measurements find that during coarsening of Nano-Porous Gold (NPG) at 300C the morphology of the gold is approximately self-similar, and that the two-phase mixtures remain bicontinuous with volume fraction of gold between 30 and 35% [3, 4], in contrast to the simluations mentioned previously. Since NPG coarsens by surface diffusion, we have determined the self-similar morphology, topology, and two-point correlations in an effort to compare to the experimental results. In addition, we have examined the stability of the bicontinuous structure at volumes fractions between 32% and 36% coarsening by either bulk or surface diffusion. We find that the self-similar morphology of the two-phase mixture coarsening by either bulk or surface diffusion at a volume fraction of 36% is considerably different from that found in the experiments. The simulations show a strong dependence on the existence of bicontinuity and morphology on the volume fraction of coarsening phase for volume fractions between 32 and 36%. These differences, and a comparison between the experimentally measured and simulated topology and two-point spatial correlations will be discussed.

References

[1] Y. Kwon, K. Thornton, P.W. Voorhees, Coarsening of bicontinuous structures via nonconserved and conserved dynamics, Physical Review E 75 (2007).
[2] Y. Kwon, K. Thornton, P.W. Voorhees, Morphology and topology in coarsening of domains via non-conserved and conserved dynamics, Philos Mag 90 (2010) 317-335.
[3] K. Hu, M. Ziehmer, K. Wang, E.T. Lilleodden, Nanoporous gold: 3D structural analyses of representative volumes and their implications on scaling relations of mechanical behaviour, Acta Mater 96 (2016) 3322-3335.
[4] M. Ziehmer, K. Hu, K. Wang, E.T. Lilleodden, A principle curvatures analysis of the isothermal evolution of nanoporous gold: Quantifying the characteristic length-scales, Philos Mag 120 (2016) 24-31.

Simulation Studies of the Mechanical Response of Nanoporous Au

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This talk presents the results of   simulation-based studies of the mechanical response of nanoporous Au structures. Computationally generated samples are utilized in combination with Embedded Atom Method (EAM) potentials.   A series of ligament sizes and solid fractions are studied in order to assess the validity of   the Gibson-Ashby scaling equations for the elastic and plastic properties of the structures.   The assessment is performed   considering the actual properties of nanowires of similar surface to volume ratios as the ligaments in the nanoporous structure. We find that the Gibson-Ashby scaling holds for solid densities higher than 50% but deviations appear for lower solid densities, due to not all the ligaments carrying the load as assumed in the scaling relations. For small ligament sizes, we find strong tension-compression asymmetry in the plastic behavior due to the effects of the surfaces. Implications of the simulations for the ductility of the nanoporous structures are also discussed.

Mechanics of Dealloyed Metal Network Structures

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Dealloying-made nanoporous metals provide model systems for studies of small-scale plasticity in the form of homogeneous metal networks with struts (ligaments) at the nanoscale. They may also lead to new structural materials which are light-weight because of the pores and strong because of the size-effect. Alloy corrosion provides a scalable preparation approach towards macroscopic bodies, made out of networks with zillions of struts. Their mechanical behavior reflects the effects of small size, of the action of capillary forces, and of the mechanics of networks with a topology that depends crucially on the phase fraction and that may depend sensibly on the processing conditions. Assessing the potential of nanoporous metals for structural applications or for integrated material systems that combine strength with function requires that these various issues are understood. These investigations are indeed feasible and rewarding, not least because the nanoporous bodies come in millimeter size dimensions and can be tested with reliable macroscopic methods, and because they are highly deformable in compression and so invite various mechanical testing schemes. Load-unload tests explore the evolution of the effective elasticity during deformation and enable links between strength and stiffness, and strain rate jump tests provide insights into local processes. Furthermore, in-situ tests of such samples in electrolyte and control of the electrode potential afford variations of the surface state during ongoing deformation processes. The response of the mechanical behavior then affords robust conclusions on the role of capillary forces in small-scale mechanics, including their impact on strength, compression-tension asymmetry, and size-dependent stiffness. The talk will provide an overview on the insights that have emerged from such studies.

Controls of microstructure to enhance mechanical properties of nanoporous gold

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To enhance mechanical properties of solid metals, defects such as grain boundary, twin boundary, and initial dislocation density are generally controlled. Simliary, we have developed processes to control microstructure in the ligaments of nanoporous gold (np-Au). we developed fabrication processes of nanocrystalline, prestrained and nanotwinned np-Au by controlling internal microstructure of precursor. Microstructures of each sample were investigated using electron microscopes before and after dealloying. Mechanical properties were measured by using nanoindentation, flexural test, compression test, and in-situ tensile test. Issues on characterizations of mechanical properties of np-Au have been studied. Time-dependent deformation of np-Au was investigated with spherical nanoindentations, and indentation size effect (ISE) in np-Au was studied. In many previous studies, it has been shown that hardness of np-Au is increased with decreasing ligament size, which is called ligament size effect, and with decreasing indentation depth, which is in line with indentation size effect (ISE) for solid materials. Regarding ISE of np-Au, there would be different mechanism from solid materials whose ISE mechanism is described with geometrically necessary dislocation because dislocations can easily glide and escape to free surface in np-Au. To discuss this, we fabricated np-Au samples with different ligament size by controlling conditions of free-corrosion dealloying and post heat treatments and investigated their structural similarity with 3D reconstruction by serial sectioning using focused ion beam. Nanoindentation, uniaxial compression and shear tests were conducted and nanomechanics modeling for indentation on np-Au is suggested to describe ISE in np-Au.

Reduction-induced Decomposition of Compounds: Self-organization towards Nanoporous Metals at Highly Incoherent Interfaces

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Like dealloying, the selective dissolution of anions from an ionic or covalent compound can also create metal and pores. The process takes place when we reduce an otherwise insoluble or sparing soluble compound with a reductant, which gives it the name reduction-induced decomposition (RID). When the conversion from the compound to the metal is accompanied by a large enough molar volume shrinkage, continuous pores evolve spontaneously. Using the RID of AgCl to Ag as a model system, we show the resemblance between structures from RID with those from dealloying. The drastically different chemistry of RID permits the fabrication of structures difficult for dealloying, including nanoporous Zn that can serve as a highly rechargeable anode. Nonetheless, the resemblance should not dwarf the differences between RID and dealloying. In fact, many RID processes investigated in our lab failed to yield nanoporous metals, which turns our attention back to the interface between the parent and the child phases, where the morphology evolution begins. The incoherency of the interface in RID may alter the atomistic path of the reaction, which is manifested in the self-organization of the metal product towards structures not yet observed in dealloying.

Lessons in glass corrosion from the dealloying of metallic systems

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For decades, there has been general agreement that corrosion is due to the combined contributions of two broad categories of mechanisms: reaction control (solution affinity, local solution changes due to secondary phase precipitation, and kinetic limitations) and transport control (ion exchange, pore tortuosity, and diffusion of rate-limiting ions). Existing models based on these mechanisms predict the resultant solution concentration of boron with reasonable accuracy, given good parameterization. They do not, however, predict (or attempt to predict) the formation of many of the structures observed at the surface of corroding glasses and often are very poor at predicting the concentrations of other ions in solution. Recently, an Energy Frontier Research Center has been formed to examine the mechanistic commonalities and differences between materials systems. In particular, the behavior of metal alloys with exposure to various fluids can provide insight into the corrosion of glass that has the potential to break this logjam. In this talk, we show how the mechanism of morphological evolution seen in corroding metal alloys can account for the dynamic structures and solution responses seen in the study of glass corrosion.

A Modified scaling law for stiffness of nanoporous materials accounting for deformation mode effects of nodes and ligaments

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Gibson-Ashby model can't well describe the stiffness of nanoporous (NP) materials as the ligament size decreases to the nanoscale. We theoretically developed a refined continuum model based on a cubic, periodic arrangement of a gyroid unit cell with three-fold node connectivity. Our modified scaling law is given as: $\frac{E}{E_s} = C_1\varphi^2 + C_2\varphi$, where C_1 and C_2 account for the bending and stretching deformation mode, respectively. We found a good agreement between the simulation and theoretical predictions of the stiffness. We identified other morphological factors such as ligament aspect ratio and node to ligament volume ratio that affect the deformation behavior of NP materials more substantially than the relative density alone. A mixture of bending and stretching modes is observed in NP materials under tensile loading. We observed a bending-dominant to stretching dominant transition for nano-sized gyroid structures with varying relative density.

Three-dimensional bicontinuous nanoporous high-entropy alloy and its sluggish coarsening

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Three-dimensional bicontinuous nanoporous (3DNP) materials demonstrate fascinating electrochemical and mechanical properties [1], but the coarsening behavior, its nature to reduce its surface energy, is an unsolved critical problem until now. We attempt to suppress the surface diffusion-based phenomenon by unique physical properties of high-entropy alloy (HEA). Recently, HEA has attracted intensive research during the past decade [2]. Unlike the conventional alloy systems based on one, rarely two, principal elements, HEA contains at least five major elements at concentrations ranging between 5 and 35 at.%. Among four 'core effects' of HEA which generate extensive research interests in the scientific community, the sluggish diffusion is the reason for the exceptional high strength and structural stability of NbMoTaW and VNbMoTaW HEAs at high-temperature [3].

In this study, TiVNbMoTa nanoporous refractory HEAs are synthesized by liquid metal dealloying (LMD) using the approach on the grounds of the enthalpy of mixing to select immiscibility elements. Using the unique LMD method of synthesizing non-noble porous metal, and by exploiting thermally activated coarsening behavior at high temperatures, this study demonstrates how effectively the sluggish diffusion of HEA can hinder the ligament growth in 3DNP structure. Transformation behavior is highly dependent on the initial chemical composition and microstructure, but the approach based on the enthalpy of mixing is successful in synthesizing porous HEAs. It is the first investigation of porous HEA, and the produced multi-component porous alloy has remarkably tiny ligaments which are one order of magnitude smaller than other general porous materials in an empirical correlation with homologous temperature ($T_{melting}$/$T_{dealloying}$). The nanoporous structure can improve chemical, physical and hybrid properties such as gas catalyst reaction, surface-enhanced Raman scattering, high yield strength, electronic transport properties by tuning the pore size down to a few nm. Therefore, our findings will shed light on studies to enhance and keep the properties of 3DNP.

1. T. Fujita *et al.*, **Nature Materials**, 11(9) (2012) 775-780.

2. J.-W. Yeh *et al.*, **Advanced Engineering Materials**, 6(5) (2004) 299-303.

3. O.N. Senkov *et al.*, **Intermetallics**, 19(5) (2011) 698-706.

Investigating the origin of macroscopic plastic flow localization of nanoporous gold thin foil during tensile deformation by in situ transmission electron microscopy
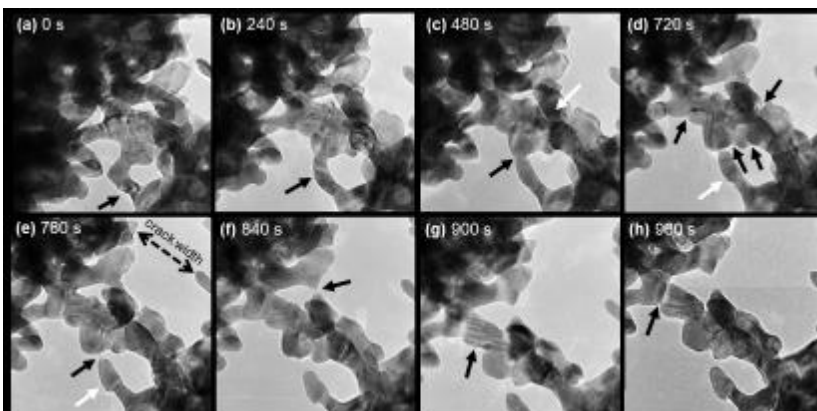
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In this presentation, we will demonstrate several different microstructure responses of a nanoporous gold (NPG) thin foil to tensile stress. This study attempts to understand the origin of plastic flow local-ization during deformation, i.e., why ductile gold exhibits a macroscopic brittle fracture behavior when it becomes a nanoporous structured material.

NPG thin foils were fabricated by dealloying 12 karat gold foil through free corrosion in 70 vol.% nitric acid for 20 minutes and then immediately rinsed in deionized water. In situ tensile experiments were performed on an FEI (now Thermo-Fisher) Titan 300 in the TEM bright field mode. A specially designed in-situ deformation specimen holder, SATO Holder Duo (Mel-Build Co., Japan) is used for in situ tensile testing.

In-situ observation was repeated several times, and then, frame-by-frame analysis of each movies were carried out to identify the deformation and fracture behaviors of individual ligaments. We as-sume that the observation of randomly chosen multiple cracks reduces the risk of overlooking disloca-tions due to the dislocation invisibility caused by the ligament's diffraction condition – the dislocation's Burgers vector orientation relationship. Most of the ligaments we observed failed through dislocation mediated {111} slip and necking without evidential dislocation interaction or dislocation density incre-ments (strain hardening). However, a few ligaments did show dislocation interaction and strain hard-ening behavior in a section before other sections began to slip and failed without showing dislocation accumulation. Figure shows the fracture behavior of a large ligament cluster. A crack width versus time plot, which measures the crack width between the two points shown by the dotted arrow in the figure. The blue dotted line approximates the crack width growth rate before the large ligament's failure and the red line approximates the rate after failure. This large ligament was single handedly slowing crack width growth and arresting propagation thus increasing the strength of the material. This evidence supports Sieradzki's theory (S. Sun et al., Nat. Mater. 14, (2015) 1-6) that NPG with a wider distribution of ligament diameters should have higher strength at the same average ligament diameter.

Nanoporous metallics for electrocatalytic reactions

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Nanoporous metals possess several distinct features that make them highly desirable as electrocatalysts. The metallic structure is interconnected resulting in a highly conductive network that allows easy transport of electrons. Additionally, the highly internal curve structure may expose various different crystal facets on the ligament surfaces which may result in favorable reaction sites depending on reaction conditions and surface composition. Also, the synthesis procedure can be applied to not only monometallic catalysts, but also bimetallic catalysts with highly porous structures and large surface areas, thus providing flexibility in creating and engineering target catalytic sites.

In this talk, I will present our work on nanoporous Ag and Cu-Ti as potential electrocatalysts for CO_2 and water electrolysis systems. Silver is an attractive CO_2 reduction electrocatalyst, because it is able to reduce CO_2 to CO with a good selectivity (~81%) and it also costs much less than other precious metal catalysts. We discovered a nanoporous silver (np-Ag) catalyst, which is able to reduce CO_2 electrochemically to CO in a highly efficient and selective way [1]. Not only the porous structure creates an extremely large surface area for catalytic reaction, but also the curved internal surface generates a large number of highly active step sites for CO_2 conversion, resulting in an exceptional activity that is over three orders of magnitude higher than that of the polycrystalline counterpart at a moderate overpotential of < 500 mV. More importantly, such a remarkable activity for CO_2 electroreduction has been achieved with a CO Faradaic efficiency of 92%.

Another example is nanoporous Cu-Ti bimetallic catalyst [2], which exhibiting an optimum hydrogen binding energy similar to that of platinum (Pt). The morphological control of material pore sets simultaneously enhanced the exposed catalytic surface area and transportation of electrolytic ions and gas bubbles; the intact metallic structure provided high-conductivity and eliminated the necessity of using supporting substrate, both of which enabled the realization of much higher mass loading for industrial application than traditional particle-based electrocatalysts.

[1] Lu, Q., Rosen, J., Zhou, Y., Hutchings, G. S., Kimmel, Y. C., Chen, J. G., & Jiao, F. A selective and efficient electrocatalyst for carbon dioxide reduction. Nat. Commun. 5:3242 (2014).

[2] Lu, Q., Hutchings, G. S., Yu, W., Zhou, Y., Forest, R. V., Tao, R., Rosen, J., Yonemoto, B. T., Cao, Z., Zheng, H., Xiao, J. Q., Jiao, F., & Chen, J. G.* Nat. Commun. 6:6567 (2015)..

Structural Disorder and Oxygen Reduction Reaction Kinetics: Friends or Foes?

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The oxygen reduction reaction (ORR) is a key reaction for energy conversion and storage systems such as polymer electrolyte membrane fuel cells (PEMFCs). Studies on Pt and Pt-transition metal alloy single crystals have established that the ORR is best electrocatalyzed on bimetallic alloys and at (111) facets. Combining alloying and ensemble effects recently led to 20-30-fold enhancement of the specific activity (normalized per real cm^2 of catalyst) for the ORR on PtNi/C nanooctahedra relative to Pt/C nanoparticles. However, due to the highly oxidizing conditions of the PEMFC cathode, the stability of PtNi/C octahedra is poor in PEMFC cathode operating conditions, thus compromising their utilization in real devices. Strikingly, it also turned out recently that structurally-disordered PtNi nanocatalysts, such as hollow PtNi/C nanoparticles, dealloyed PtNi/C nanoparticles, PtNi aerogels or PtNi nanowires feature highly desirable and sustainable ORR activity (x 10-12 in specific activity relative to pure Pt/C). However, to date, the mechanisms of this unexpected ORR activity enhancement remain unclear, and prevent further development of this vital technology for a carbon-free energy future.

To shed fundamental light onto these issues, state-of-the art PtNi/C nanocatalysts with distinct atomic composition, size, shape and density of disorder were synthesized. Their disorder was quantified experimentally, using the values of microstrain (a parameter accessible by the Rietveld refinement of wide-angle X-ray scattering patterns) that is representative of the local distortion of a crystal lattice. Thanks to *ab initio* calculations, the contributions of bulk and surface structural disorder were disentangled, and a new parameter, the surface distortion (SD), was established. The SD descriptor was used to rationalize the ORR activity enhancement of the two classes of materials (structurally-ordered and structurally-disordered), and to probe their stability in simulated PEMFC cathode operating conditions.
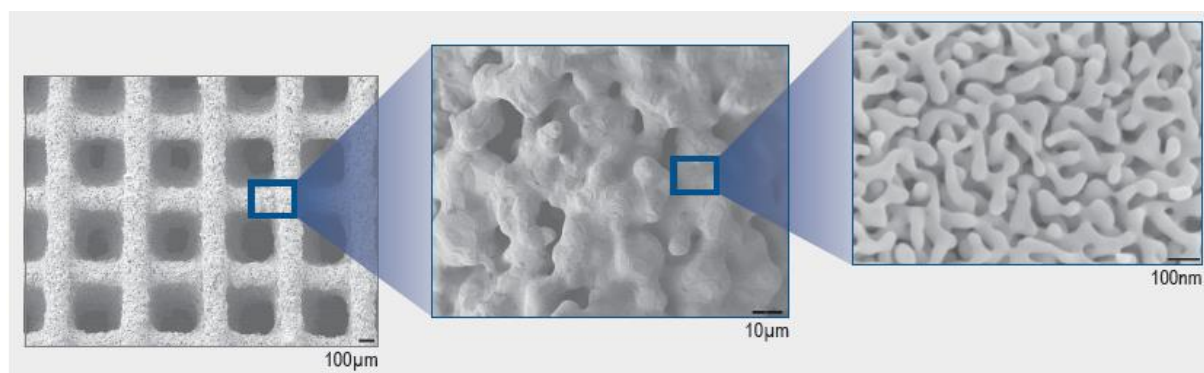
R. Chattot, O. Le Bacq, V. Beermann, S. Kühl, J. Herranz, S. Henning, L. Kühn, T. Asset, L. Guétaz, G. Renou, J. Drnec, P. Bordet, A. Pasturel, A. Eychmüller, T. J. Schmidt, P. Strasser, L. Dubau, F. Maillard, "Surface Distortion as a Unifying Concept and Descriptor in Oxygen Reduction Reaction Electrocatalysis", Nat. Mater. 17 (2018) 827-833. DOI: 10.1038/s41563-018-0133-2

Dealloying Derived Nanoporous Architectures for Improved Mass Transport

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Monolithic nanoporous metals, derived from dealloying, possess a unique bicontinuous solid/void structure that provides both large surface area and high electrical conductivity, making them ideal candidates for various energy applications. On the other hand, their performance is often limited by slow mass transport through their nanoporous architecture. Thus many potential applications would greatly benefit from the integration of an engineered macroporous network structure that facilitates and directs the application specific mass transport. One way to realize such structures is to 3D print precursor alloy structures with engineered non-random macro-architectures followed by dealloying to generate nanoporosity for high surface area. Recently, we demonstrated this approach for 3D printed hierarchical nanoporous gold (3DP-hnp-Au) [1]. The material exhibits three distinct structural length scales ranging from the digitally controlled macroporous network structure (10-1000 μm) to the nanoscale pore/ligament morphology (30-500 nm) controlled by dealloying. Supercapacitance, pressure drop, and catalysis measurements all demonstrate that integration of the 3D macropore network improves mass transport and reaction rates for both liquids and gases. For applications that don't require monolithic samples as, for example, catalysis ball milling of brittle intermetallic precursor alloys provides another avenue to improve the utilization of the material.

[1]   C. Zhu, Z. Qi, V. A. Beck, M. Luneau, J. Lattimer, W. Chen, M. A. Worsley, J. C. Ye, E. B. Duoss, C. M. Spadaccini, C. M. Friend, J. Biener, *Science Advances* **2018**, *4, eaas9459*.

Emerging Non-Precious Nanoporous Materials for Alkali-ion Batteries and Hydrogen Energy Technologies
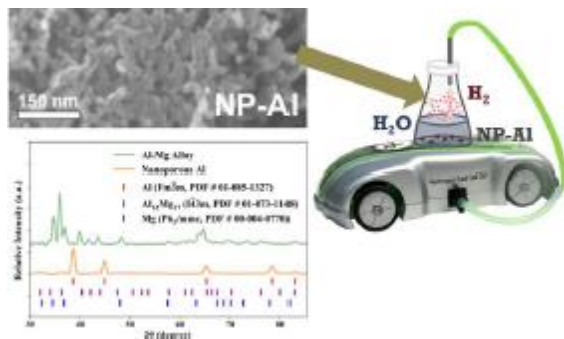
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Dealloyed nanoporous materials are expected to play a key role in meeting the energy challenges of the 21st century, owing to their promising applications in (electro)catalysis,[1] electrochemical energy conversion and storage,[2,3] energy-efficient actuators,[4] gas storage and CO2 capture. In the first part of this talk, I will present the performance of non-precious nanoporous materials made by selective alloy corrosion including nanoporous antimony (NP-Sb)[2] and nanoporous tin (NP-Sn)[3] as emerging high-capacity Na-ion and Li-ion battery anodes.

Over 95 % of hydrogen used worldwide is produced by steam reforming of natural gas, which is not a sustainable method since CO2 is co-produced during steam reforming. In the second part of this talk, I will present a novel air-free synthesis route to hierarchical nanoporous aluminum (NP-Al) for on-board hydrogen generation by hydrolysis with pure water to feed fuel cells.[5,6] Thanks to a new carbon-free sustainable pathway to extract aluminum by Elysis (https://elysis.com/en), a joint venture composed of high-profile aluminum suppliers including Rio Tinto and Alcoa, and aluminum consumers including Apple, aluminum could be obtained by electrolysis of Al_2O_3 without CO_2 emissions. The inclusion of this carbon-free aluminum in our dealloying process will make it possible to produce hydrogen from nanoporous aluminum and pure water without greenhouse gas emissions at any stage of the process.[5,6]

[1] E. Detsi* J. B. Cook, B. Lesel, C. Turner, Y.-L. Liang, S. Robbennolt and S.H. Tolbert. Energy & Environ. Science 9, (2016).

[2] O. Ruiz, M. Cochrane, M. Li, Y. Yan, K. Ma, J. Fu, Z. Wang, S.H. Tolbert, V.B. Shenoy and E. Detsi* Advanced Energy Mater 8, (2018). [3] E. Detsi* X. Petrissans, J.B. Cook, Y.-L. Liang, Z. Deng, B. Dunn and S.H. Tolbert. Physical Review Materials 2, 055404 (2018).

[4] Q. Bai, Y. Wang, J. Zhang, Y. Ding, Z. Peng and Z. Zhang, Journal of Mater. Chemistry C 4, (2015).

[5] J. S. Corsi, J. Fu, Z. Wang, and E. Detsi*: (Under review)

[6] E. Detsi* and J. S. Corsi. Patent Application, #18-8558-104377.000203

Processing-Structure Correlation in Dealloying by Aqueous Solution, Liquid Metal and Solid-State Diffusion by X-ray Microscopy and Spectroscopy

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Dealloying, a selective etching process, can be used to fabricate a variety of nanoporous metals with a characteristic bi-continuous structure. The bi-continuous patterns did not exist in the alloy prior to the dealloying process, but rather formed dynamically via an elegant self-organizing process while the dealloying progressed. The most widely studied dealloying method is aqueous solution dealloying (ASD). Instead of an aqueous solution, a molten liquid metal can be used in dealloying and phase separation, so-called liquid metal dealloying (LMD). Alternatively this phase separation and transformation process, utilizing a metal as the dealloying agent to form bi-continuous structure, can also be achieved by a solid-state interfacial dealloying (SSID). Our work includes addressing the processing-structure correlation in the three different dealloying systems, in particular utilizing advanced synchrotron-based imaging/microscopy and spectroscopic methods; these include X-ray nano-tomography, nano-probe X-ray fluorescence microscopy, and spectroscopic imaging. We will discuss the different dealloying systems to shed light on their underlying mechanisms.

Morphological Control during Liquid Metal Dealloying

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Liquid metal dealloying (LMD) is by now an established technique to produce nanocomposite and open nanoporous structures with ultra-high interfacial area for diverse applications. However, the complex interfacial pattern formation mechanisms that yield a rich variety of structures remain incompletely understood. This talk will present results of combined phase-field modeling and experimental studies that explore how LMD morphologies can be controlled by varying the liquid melt composition. We examine the generic cases where the liquid melt contains the miscible element of the base alloy, exemplified by dealloying Ta-Ti alloys by Cu-Ti melts, and where the liquid melt contains a different element that reduces the solubility of the miscible element in the melt, exemplified by dealloying of Ta-Ti alloys by Cu-Ag melts. We find that both Ti and Ag addition in the melt slow down dealloying kinetics and enhance morphological instability at the dealloying front so as to promote the formation of a topologically connected structure over a larger range of base alloy composition so as to extend the formation of topologically connected structures to smaller volume fraction of the Ta rich phase. Furthermore, Ag addition slows down coarsening kinetics to form structures with smaller and spatially more uniform ligament width, while Ti addition has the opposite effect of speeding up both coarsening and dissolution of the dealloyed structure. Those results open up new possibilities for using melt composition control during LMD to produce nanocomposite and nanoporous structures with desired compositions and morphologies.

Structural evolution of nanoporous metals: an in-situ TEM study

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Dealloyed nanoporous metals are characterized by a unique combination of mechanical rigidity, clean surface, and flexible nanoporosity. These structural features are particularly suitable for high space resolution characterization techniques, such as spherical aberration corrected TEM/STEM, discrete tomography, and in-situ TEM, which provide in-depth evidences to elucidate their structure-property correlation under realistic operating conditions. This talk will focus on our recent in-situ TEM studies (in-situ heating, in-situ catalysis, etc) on several nanoporous metals, which reveal some interesting phenomena.

Real-time USAXS and WAXS studies of morphology evolution in 3D nanoporous gold during electrochemical dealloying and Post-Dealloying Coarsening

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In this talk, I will present a fundamental study on microstructural and crystallographic evolution during electrochemical dealloying and post-dealloying coarsening by combining in situ and operando Ultra Small Angle X-Ray Scattering (USAXS) and Wide Angle X-Ray Scattering (WAXS) experiments that we have developed to measure structural change on several length scales in real time.[1] The experiments were realized with the simultaneous WAXS/USAXS capability of the University of Pennsylvania's multi-detector Dual Source and Environmental X-Ray Scattering (DEXS) facility. Soyarslan and co-workers have investigated the morphological and topological similarities of nanoporous gold and Cahn's spinodal decomposition model based on a computed Gaussian Random Field.[2,3] By fitting WAXS/USAXS curves with this model, we can both visually reconstruct (see Figure 1), and map material properties to (specific surface area, pore fraction, ligament and grain size), the sample as it evolves under both electrochemical and thermal treatments.
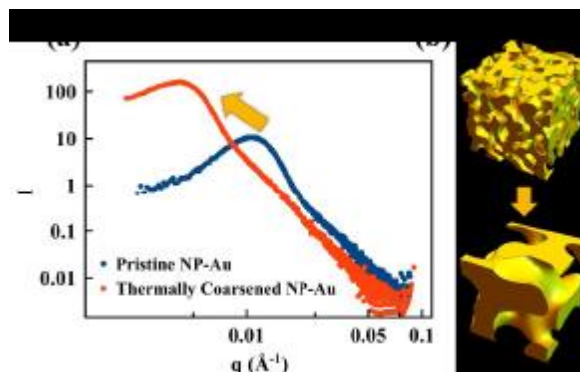

Figure 1. (a) Typical scattering curves of nanoporous gold as it evolves under thermal coarsening. (b) Visual reconstruction of the porous structure before and after coarsening (side length of both cubes is 330 nm).

References

1. Welborn, S.S. & Detsi, E: Small-Angle X-Ray Scattering of Nanoporous Metals. Nanoscale Horiz.(Invited paper in preparation).
2. Cahn, J. W. Phase Separation by Spinodal Decomposition in Isotropic Systems. J. Chem. Phys. 42, 93–99 (1965).
3. Soyarslan, C., Bargmann, S., Pradas, M. & Weissmüller, J. 3D stochastic bicontinuous microstructures: Generation, topology and elasticity. Acta Mater. 149, 326–340 (2018).

Fracture toughness of nanoporous gold with hierarchical grain structure

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Nanoporous gold (np-Au) is a material with sponge-like structure, composed of continuous ligament and pore at the nanoscale. Due to low density and high surface area-to-volume ratio, there have been many researches to apply np-Au as catalyst, actuator, and sensor. However, brittle behavior of np-Au unlike ductile gold at bulk scale remains as an issue to be overcome. Previous researches have shown that the brittleness of np-Au appears by stress concentration on pore surface and catastrophic crack propagation through grain boundary, which had been formed under Au-Ag precursor alloy state. Here, we focus on crack propagation through the grain boundary and investigate dependency of fracture toughness on grain boundary structure. We fabricated well-annealed, cold-rolled, and hot-rolled Au-Ag precursor alloys. Well-annealed precursor alloys had grain size of micro-scale, cold rolled precursor alloys had grain size of nano-scale, and hot rolled precursor alloys had anisotropic grain structure with grain size of micro-scale. By free corrosion dealloying in nitric acid, Ag is selectively etched from pre-cursor alloy and np-Au is formed with grain boundary structure of well-annealed, cold-rolled, and hot-rolled precursor alloy. Microstructure of precursor alloys and np-Au were observed by SEM (scanning electron microscope) and EBSD (electron back-scattered diffraction). Dependency of fracture tough-ness, KIc on grain boundary structure is investigated under tension with nano-UTM, and effect of grain boundary density and grain boundary structure on fracture toughness and crack propagation path are discussed.

Verifying Larché-Cahn theory by measuring open-system elasticity of nanoporous palladium(-gold)-hydrogen

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Monolithic nanoporous metals with large surface-to-volume ratio are suitable for studying the mechanical behavior of nanostructured metals via conventional, macroscale mechanical testing ap-proaches. Nanoporous gold is usually the model system of choice. Most recently, we established the synthesis of monolithic and uniform bodies of nanoporous palladium (np Pd) as an alternative and explored the mechanical responses of this material through electrochemically controlled hydrogen sorption [1-3]. Here, we report the synthesis of monolithic nanoporous palladium and palladium-gold (Pd-Au) samples by electrochemically dealloying Cu85Pd15 and Cu85Pd12.5Au2.5, respectively. Both na-noporous materials show ligament sizes below 10nm, which allow fast hydrogen diffusion or redistri-bution across their diameter when stress gradients are induced by bending. The Young's modulus var-iation of np Pd and Pd-Au during hydrogen absorption/desorption are measured by a dynamic me-chanical analyzer. It is found that hydrogen sorption induced more than 30% reversible compliance variation in np Pd, suggesting new opportunities in the design of functional materials with switchable elastic stiffness. Moreover, experimentally measured elastic coefficients of H-diluted np Pd(-Au)-H sin-gle-phases show excellent agreement with the prediction by the Larché-Cahn theory of open-system elasticity. Our experiments provide the first direct verification of the Larché-Cahn theory as a mile-stone of 20th-century thermodynamics.

References

1. S Shi, J Markmann, J Weissmüller. Actuation by hydrogen electrosorption in hierarchical nanopo-rous palladium. Philosophical Magazine 97 (2017) 1571-1587.

2. S Shi, J Markmann, J Weissmüller. Synthesis of uniform bulk nanoporous palladium with tunable structure. Electrochimica Acta 285 (2018) 60-69.

3. S Shi, J Markmann, J Weissmüller. Verifying Larché–Cahn elasticity, a milestone of 20th-century thermodynamics. Proceedings of the National Academy of Sciences 115 (2018) 10914-10919.

Nanoporous Aluminum: synthesis and mechanical properties

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The porous aluminum (or foam Al) has been widely used in many areas of the modern industry. But preparing nanoporous Al by dealloying is still challenging because Al is too reactive in aqueous solutions. Here we present that the nanoporous Al (np Al) can be prepared by combining dealloying and galvanic replacement reaction (GRR) in an ionic liquid electrolyte.1 While Mg in an Al2Mg3 alloy was galvanically replaced with Al in an ionic liquid, the Al2Mg3 was dealloyed to form a np Al framework and meanwhile the reduced Al was deposited into the pores and uniformly plated on the ligament surface. It leads to crack-free, high density, and mechanically stable np Al samples. We found that their structure is stable up to the melting temperature of Al, benefiting from a thin passive layer of oxide on ligament surface. We will also present experimental results on mechanical properties (hardness, tensile properties) of the nanoporous Al and compare it with the data of the nanoporous Au.
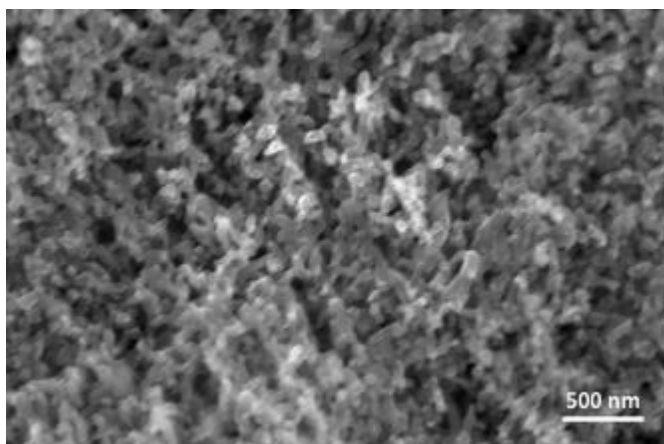

Figure 1. SEM image of nanoporous Al prepared by dealloying/GRR procedure.
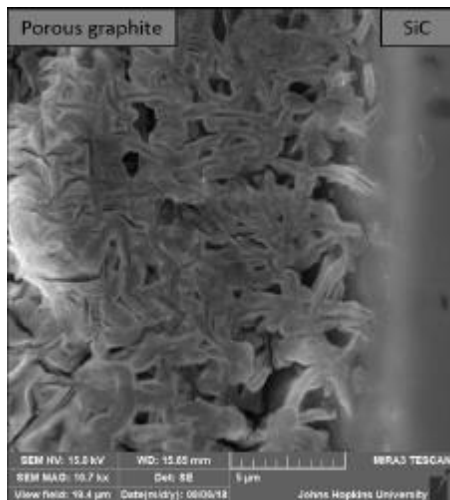
References

1. W. Yang, X.-G. Zheng, S.-G. Wang and H.-J. Jin, Journal of the Electrochemical Society 165, C492 (2018).

Synthesis of Porous Graphite by Dealloying of Silicon Carbide

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Liquid metal dealloying is a well-established technique used to produce a variety of porous materials from an initially homogeneous alloy. While this method has been used previously to fabricate bi-continuous porous graphite via the selective dissolution of Mn from a Mn-C precursor [1], we have prepared a porous graphitic structure using a ceramic precursor, instead of a metal containing alloy. Here, a sliver of an N-doped 4H SiC wafer was immersed in a bath of liquid Ge, resulting in a fully dense carbon and Si/Ge composite. Upon removal of the Ge phase, porous graphite remained whose features resembled that of nanographite [2], i.e., nano-crystalline graphite with many edge defects and a Raman spectrum that featured an ID/IG ratio of 0.5. We will discuss the kinetics of dealloying as well as the morphology of carbon obtained by dealloying different polytypes of SiC. This novel method of preparing porous graphite can be useful in the fabrication of electrode and capacitor materials.

References

1. S.-G. Yu, K. Yubuta, T. Wada, and H. Kato, "Three-dimensional bicontinuous porous graphite generated in low temperature metallic liquid," Carbon N. Y., vol. 96, pp. 403–410, Jan. 2016.

2. M. A. Pimenta, G. Dresselhaus, M. S. Dresselhaus, L. G. Cançado, A. Jorio, and R. Saito, "Studying disorder in graphite-based systems by Raman spectroscopy," Phys. Chem. Chem. Phys., vol. 9, no. 11, pp. 1276–1290, Mar. 2007.

Ligament size effect in strength of nanoporous gold in tensile and compressive loading

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Ligament-size-dependent strength in np-Au, strength increases with decreasing ligament size like as size effect in nanopillars, has been studied extensively. Many studies on ligament size effect were carried out with nanoindentations having the advantage of experimental convenience, but converting from hardness measured by nanoindentation to strength has been controversial. Although there have been a few studies related with ligament size effect investigated by tensile or compressive tests, systemic analysis on deformation of np-Au in both tensile and compressive loading is not fully carried out. In this study, we investigated the effect of ligament size of np-Au on tensile and compressive behavior. By preparing micro-scale samples without grain boundaries and micro-cracks that can be introduced in macro-scale samples, we could focus on effect of ligament size only. We prepared four coarsened np-Au samples with average ligament size of 56, 149, and 402 nm by free corrosion dealloying and post heat treatments. Tensile and compressive samples were prepared by focused ion beam (FIB) and the mechanical tests were performed using in-situ push-to-pull (P-to-P) devices for tensile testing, and with the nanoindenter installed with flat punch tip for compressive testing. We found ligament size effects in both tensile and compressive loading, but size effect exponents, n in $\sigma = Ad^{-n}$ where σ is the strength, A is the coefficient, and d is the ligament size, are different for tensile and compressive loading. We discuss the effect of loading mode on deformation and size effect in strength.

Enhanced tensile strength of nanotwinned nanoporous gold

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Twin boundaries are effective microstructural defects for enhancing the strength of materials at multiple scales. Twin boundaries are mirror planes in the crystallographic lattice with perfect coherency and serve as strong barriers to dislocation motion and slip transfer, resulting in high strength. The mechanical fragility of np-Au is fundamentally attributable to its low tensile strength, which is caused by its irregular open-cell structures and results in catastrophic failure under tension. Stress gets con-centrated at the weak parts of the load-bearing ligaments when the material is subjected to an external tensile force. Thus, strength of np-Au could get increased by enhancing yield stress of load-bearing ligaments with introducing nanotwin structure in ligaments. We fabricated nanotwinned nanoporous gold (nt np-Au) thin film and measured its mechanical properties using in-situ tensile testing. We fab-ricated twinned and textured np-Au foils with an average twin spacing of 7.9 nm. The foils exhibit an ultimate tensile strength (UTS) of 87.5MPa when the loading axis is normal to the twin boundaries. This UTS value is approximately three times greater than that for np-Au with rare twins of 27.4 MPa due to strain-hardening of nanotwin barriers in load-bearing ligaments. [1]

References

1. Gwak, E. J., Jeon, H., Song, E., Kang, N. R. & Kim, J. Y. Twinned nanoporous gold with enhanced tensile strength. Acta Mater. 155, 253-261 (2018).

Sequence-Specific Electrochemical Detection and Purification of Nucleic Acids with Nanoporous Gold Electrodes

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Nucleic acid-based biosensors have enabled rapid and sensitive detection of pathogenic targets; however, these devices often require purified nucleic acids for analysis since the constituents of complex biological fluids adversely affect sensor performance. This purification step is typically performed out-side the device, thereby increasing sample-to-answer time and introducing contaminants. We report a novel approach using a multifunctional matrix, nanoporous gold (np-Au), which enables both detection of specific target sequences in a complex biological sample and their subsequent purification1,2. The np-Au electrodes modified with 26-mer DNA probes (via thiol-gold chemistry) enabled sensitive detection with a tunable dynamic range and capture of complementary DNA targets in the presence of complex media (fetal bovine serum) and other interfering DNA fragments in the range 50 to 1500 base pairs1-3. Upon capture, the non-complementary DNA fragments and serum constituents of varying sizes were washed away. Finally, the surface-bound DNA-DNA hybrids were released by electrochemically cleav-ing the thiol-gold linkage and the hybrids were iontophoretically eluted from the nanoporous matrix. The optical and electrophoretic characterization of the analytes before and after the detection-purifica-tion process revealed that low target DNA concentrations (80 pg/μL) can be successfully detected in complex biological fluids and subsequently released to yield pure hybrids free of polydisperse digested DNA fragments and serum biomolecules. Taken together, this multifunctional platform, coupled with electrochemically-generated np-Au morphology libraries to rapidly determine optimal electrode mor-phologies3, is expected to enable seamless integration of detection and purification of nucleic acid bi-omarkers in miniaturized diagnostic devices for point-of-care applications.
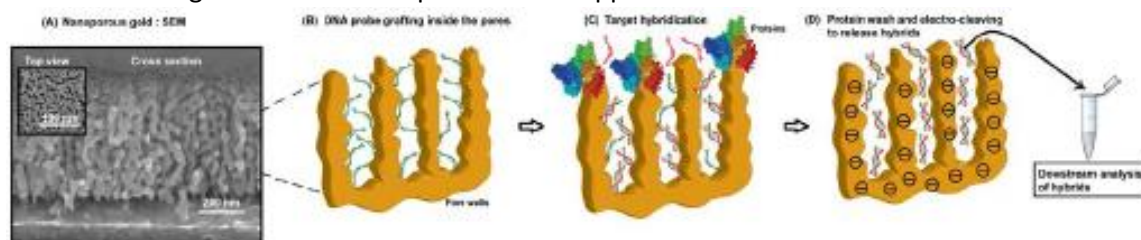

Figure 1. (A) Scanning electron micrographs of np-Au electrode. (B) Thiol-immobilized ssDNA capture probes inside the porous structure. (C) Selective transport of target molecules into the pores while macromolecules (e.g., proteins and other components of FBS) are blocked at the pore entrances. (D) Protein wash and electrochemical cleaving of DNA-DNA hybrids in a low ionic strength buffer. Downstream analysis of eluted hybrids via fluores-cence (hybrid concentration), absorbance (DNA-to-protein concentration ratio), and capillary electrophoresis (hy-brid size and purity).

References

1. Daggumati, P., Appelt, S., Matharu, Z., Marco, M.L., Seker, E., "Sequence-specific electrical purification of nucleic acids with nanoporous gold electrodes," Journal of the American Chemical Society 138:7711 (2016).

2. Matharu, Z., Daggumati, P., Wang, L., Dorofeeva, T.S., Li, Z., Seker, E., "Nanoporous gold-based electrode morphology libraries for investigating structure-property relationships in nucleic acid-based electrochemical biosensors," ACS Applied Materials & Interfaces 9:12959 (2017).

3. Daggumati, P., Matharu, Z., Seker, E., "Effect of nanoporous gold thin film morphology on electrochemical DNA sensing," Analytical Chemistry 87:8149 (2015).

ON- and OFF-Switching of Ferromagnetism in Nanoporous Pd(Co)

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In the present work the particular features of dealloyed, nanoporous (np) metals have been exploit-ed to switch magnetism. Besides the pore and ligament morphology itself, residues of the initial alloy affect the overall properties of np metals. During the dealloying process, parts of the base alloy are buried under nobler alloy atoms inside the ligaments. Ultimately, this leads to a cluster distribution of the remnant base alloy inside the np network, which sensitively depends on the initial dealloying parameters [1, 2].

In this work, residual clusters of cobalt in np palladium are utilized for the magnetic functionalization of the entire structure. Palladium as a d-band metal is on the verge of ferromagnetism, considering its electronic structure. Low amounts of magnetic impurities, such as 0.1 atomic percent of (dis-persed) cobalt atoms were found to be enough to turn the cobalt-palladium alloy into a ferromagnet at low temperatures[3]. Dealloying of CoPd (initial composition Co75Pd25) allows to adjust the cobalt concentration and distribution, so that the materials get prone to ferromagnetism at ambient tem-perature. High-resolution TEM in combination with elemental mapping techniques revealed a residu-al cobalt concentration of about 8 at% agglomerated in clusters with an average size of 1.5-2 nm.

Our motivation was to start in the paramagnetic state of np Pd(Co) and to drive it into ferromag-netism by electrochemical stimuli. For that purpose an in situ electrochemical cell for the use in a SQUID-magnetometer was constructed. Hydrogenation of palladium in that cell proved to be an ideal reaction to achieve a reversible on- and off-switching of ferromagnetism. The high surface-to-volume ratios of np palladium were particularly advantageous for fast reaction kinetics. Magnetic hysteresis measurements revealed a substantial enhancement of both saturation magnetization and coercivity upon hydrogen treatment, which clearly indicates ferromagnetic behavior. Constant field measure-ments upon voltammetric cycling support these experimental findings by changes in the net magnet-ization of more than 800%. Our results are discussed in terms of magnetic interactions between the superparamagnetic cobalt clusters and a magneto-elastic coupling in the expanded palladium lattice upon hydrogenation.

References

1. T. Krekeler, A. V. Straßer, M. Graf, K. Wang, C.Hartig, M. Ritter, J. Weissmüller, Silver-rich clusters in nanoporous gold, Materials Research Letters, 5, 314-321 (2017)
2. X.-L. Ye, N. Lu, X.-J. Li, K. Du, J. Tan, and H.-J. Jin, Primary and Secondary Dealloying of Au(Pt)- Ag: Structural and Compositional Evolutions, and Volume Shrinkage, Journal of The Electro-chemical Society, 161, C517-C526 (2014)
3. R. M. Bozorth, P. A. Wolff, D. D. Davis, V. B. Compton, J. H. Wernick, Ferromagnetism in Dilute Solutions of Cobalt in Palladium, Physical Review, 122, 1157-1160 (1961)

Leveraging Nano-scale Physics for Nanoporous Gold Based Gas Sensing

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Gas sensors are a core tool in maintaining safety in research and industrial environments. Gas sensors must not only provide robust measurements, but also be able to discriminate accurately between different chemicals. While nanoporous metals have been extensively used in aqueous chemical sensing, only limited research exists in their potential as a gas sensor. By leveraging different nano-scale phenomena, multi-variate gas sensing is possible through changes in the electrical properties of nanoporous metals.

It is well understood that the many physical properties, including electrical resistance, of nanoporous metals are dependent on adsorbed surface compounds [1]. Volatile compounds will adsorb to surfaces and form a thin surface layer- the degree of coverage is dependent on the partial pressure [2]. We show that changes in the gas concentration of different volatile compounds are transduced by nanopo-rous metals into changes in the electrical resistance.

Perhaps more interesting is the observed change in the capacitive behavior of nano-porous metals when exposed to different vapor environments. We postulate that this change in stored charge is driven by condensed liquid in the nano-pores. This condensation can occur below the typical saturation pressure due to confined curvature of nano-pores [3]. As vapor condenses into liquid, the ability for the charges to accumulate on the surface changes. These changes were reflected in measurements of the electrical reactance. By combining such data with changes in electrical resistance, we demonstrate robust and selective gas sensing. This independent novel sensing mechanism highlights the unexplored potential of nanoporous metal gas sensors.

References

1. P. Wahl, T. Traußnig, S. Landgraf, H.-J. Jin, J. Weissmüller, and R. Würschum, "Adsorption-driven tuning of the electrical resistance of nanoporous gold," Journal of Applied Physics, vol. 108, no. 7, p. 073706, Oct. 2010.

2. M. Hakamada, N. Kato, and M. Mabuchi, "Electrical resistivity of nanoporous gold modified with thiol self-assembled monolayers," Applied Surface Science, vol. 387, pp. 1088–1092, Nov. 2016.

3. F. Casanova et al., "Gas adsorption and capillary condensation in nanoporous alumina films," Nanotechnology, vol. 19, no. 31, p. 315709, Aug. 2008.

Nanoporous Gold reveals the Origin of Photoelectrons injected into Hydrogen Evolution Reaction

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Due to its broadband absorption properties and its structural tunability, nanoporous gold (npAu) represents an attractive material to investigate and improve photocatalytic reactions such as water splitting or glucose oxidation. Thin films of npAu samples exhibit remarkable optical absorption that can be increased when the ligaments are decreased in size. The absorption of light leads to an ener-getic elevation of electrons in the metal upon their collisions either in the bulk (collisions with defects or phonons) or at the surface. We demonstrate how such "hot" electrons are injected into an adja-cent phase. In our case this is a protic electrolyte where they enhance electrochemical hydrogen evolution reaction (HER). With respect to the injection efficiency the origin of the electron (surface vs. bulk) represents a decisive determinant because surface-generated electrons will not be subject to scattering events in the bulk which are responsible for energy loss and hot electron decay. In order to prove and quantify a volume-to-surface transition of photoelectron generation, the illuminated volume of the nanocrystal must be kept constant while decreasing their size. For Au nanoparticles, however, this can hardly be achieved because the quantitative determination of charge carrier ex-change requires for a current measurement with an electrical contact and no barrier layers (i.e. no ligand molecules). In contrast, npAu structures are self-similar over a wide range of ligament widths, i.e. the absorbing volume will not change while ligaments are changed in diameter. Apart, typical ligament widths cover exactly the range between full optical absorption (< 100 nm) and the mean free path for electrons in a defect-free nanocrystal (> 5 nm). This talk is therefore aiming on demon-strating that npAu, when used as a photoelectrode, can help identifying the volume-to-surface tran-sition to exhibit strong surface effects at approximately < 30 nm crystal diameter. This finding helps in designing and identifying new and more efficient photocatalyst materials based on nanoporous metals.

Evolution of Nanoporosity upon Thermal Decomposition of Transition Metal Dichalcogenides

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Development of nanoporosity on metals and alloys is a well-known pathway for making three dimensional high surface area structures especially useful for catalysis[1]. Majority of the techniques has been based on selective removal of a sacrificial metal from an alloy, a method known as dealloying. The driving force for the traditional electrochemical/chemical dealloying is difference of redox poten-tials and dissolution tendencies amongst the constituent metals. This limits the process to few noble metals[2] e.g. Pt, Pd, Au etc. that can make homogeneous alloys with less noble metals. More recently liquid metal dealloying[3] and vapor phase dealloying[4] have been also identified to mimic the process of traditional dealloying based on difference of affinities of thermal dissolution in a liquid metal, and vapor pressures of the constituent metals, respectively. However, these are still restricted to few metals and the primary challenges lie with obtaining homogeneity in precursor alloy and limiting the pore size within 100 nm upon spinodal decomposition. Here, we present gas phase thermal decom-position of transition metal dichalcogenides (TMDs) as an alternative to dealloying that generates nanopores for a broader class of metals including refractory metals like W, Mo, Re etc. The chalcogen is removed from the surface by both reductive reaction with hydrogen and evaporation at elevated temperatures, which leads to the rearrangement and surface diffusion of the remaining metal atoms that evolve into an interconnected bicontinuous nanoporous network. The length scales of the pores can be tuned by decomposition time, temperature and for some, by changing the identity of the chalcogen. Based on varying dynamics of pore formation and residual chalcogen contents for different TMDs, we have also proposed a mechanism that emulates the decomposition process. The avail-ability of vast library of TMDs having inherent atomistic homogeneity makes it a universal technique that can be utilized to make nanoporous metals.

References

1. Luc, W. & Jiao, F. Nanoporous Metals as Electrocatalysts: State-of-the-Art, Opportunities, and Challenges. ACS Catal. 7, 5856–5861 (2017).
2. Zhang, Z. et al. Generalized fabrication of nanoporous metals (Au, Pd, Pt, Ag, and Cu) through chemical dealloying. J. Phys. Chem. C 113, 12629–12636 (2009).
3. Wada, T., Yubuta, K., Inoue, A. & Kato, H. Dealloying by metallic melt. Mater. Lett. 65, 1076–1078 (2011).
4. Lu, Z. et al. Three-dimensional bicontinuous nanoporous materials by vapor phase dealloying. Nat. Commun. 9, (2018).

3D Microporous Carbon by Room-Temperature Chemical Dealloying of Metallic Carbides

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Top-down dealloying has been demonstrated to be one of the most effective ways to fabricate 3D bicontinuous porous materials. A wide spectrum of nanoporous metals, alloys and compounds with tunable porosity and pore sizes have been fabricated. However, the synthesis of nanoporous carbon materials has rarely been explored. Though liquid metal dealloying has been used for the preparation of porous graphite, the resultant materials usually have length scales over 100 nm and do not have appreciable uniformity. Here, we report the fabrication of 3D nanoporous carbon with uniform bicontinuous porosity in the micropore range by facile room-temperature chemical dealloying of metallic carbides. The small morphological length scale of ~0.55 nm well correlates with the low 'homologous dealloying temperature' and would represent the smallest pore size that can be achieved with nanoporous materials by dealloying. In addition, the average pore size can be tuned through the composition of metallic carbide precursors. Using a 3D mesoporous carbide precursor, a hierarchical meso-/micro-porous carbon has been synthesized with enhanced mass transport property for high-rate electrochemical Na$^+$ storage.
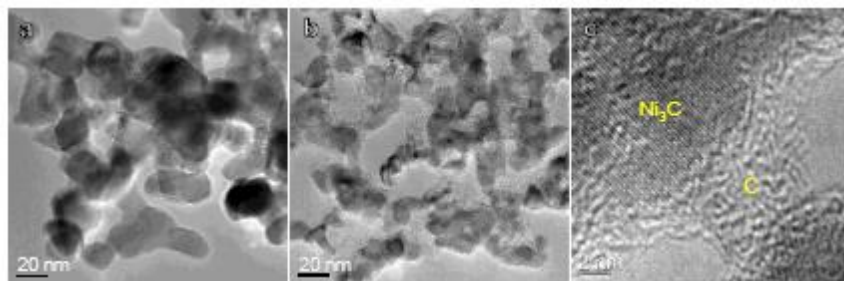
Figure 1. (a) TEM image of Ni$_3$C precursor; (b,c) TEM images of partially dealloyed Ni$_3$C at low and high magnifications.

Bicontinuous structure by reversing peritectic reaction: is it dealloying?

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The bi-continuous structure can be formed either by (electro-) chemical dealloying,[1] or by liquid metal dealloying[2-4] even vapor phase dealloying processes5. Although the mechanisms of the mass transport in these processes are quite different, there are two common features that might be the key to the formation of a bi-continuous structure: the first is that it involves a transformation where a solid phase decomposes into another solid phase and a fluid phase (liquid or gas); and the second is that the reaction proceeds by moving the reaction boundary from one side to the other (from surface to the interior). A question then arises as: whether it be possible to trans-form a single-phase material into a bi-continuous bi-phase structure, simply by thermal treatments if the above requirements can be fulfilled. We found that this strategy works well when a peritectic reaction is reversed and it proceeds in a directional way. With this approach, a TiAg intermetallic compound can be decomposed into a bi-continuous structure of liquid Ag and solid Ti framework, above the peritectic point. Quenching it to room temperature lead to a bi-continuous Ti-Ag alloy (see Figure). Compared with conventional dealloying processes, our method does not involve mass exchange between the sample and the environment. Our approach also differs from spinodal decomposition, which happens in a limited number of alloys.
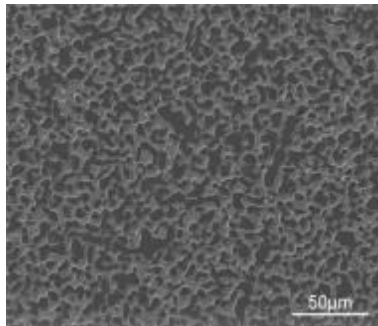

Figure 1. SEM image of a bi-continuous Ti- Ag alloy prepared by inverse peritectic reaction. Dark phase: Ti; Bright phase: Ag.

References

1. Erlebacher J, Aziz M J, Karma A, et al. Nature, 2001, 410(6827):450-3.
2. Wada T, Yubuta K, Inoue A, et al. Materials Letters, 2011, 65(7):1076-1078.
3. I. McCue, B. Gaskey, P.A. Geslin, A. Karma, J. Erlebacher, et al. Acta Mater. 115 (2016)10-23.
4. Okulov I V, Okulov A V, Volegov A S, et al. Scr. Mater, 2018, 154:68-72.
5. Lu Z, Li C, Han J, et al. Nature Communications, 2018, 9(1):276.

The Fabrication of Nanoporous Zn via Reduction-induced Decomposition

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Reactive metals with nanoporous structure, like nanoporous Zn, have potential applications in energy storage. However, it is difficult to fabricate nanoporous reactive metals by dealloying because of the oxidative nature of the process. To prepare nanoporous reactive metal, the dissolving component in dealloying needs to be much more reactive. Therefore, for nanoporous Zn, we will need alloys like LiZn or NaZn. These alloys have limited miscibility, and they are difficult to fabricate with a high homogeneity. Instead, reduction-induced decomposition (RID)[1,2] of metal compounds could readily achieve nanoporous reactive metals. We will show that the RID of Zn compound precursors can lead to a uniform nanoporous Zn structure of 100 nm wide ligaments and >80% porosity. The structure partly retains the shape of the precursor. We will also discuss the application of the nanoporous Zn anode in a rechargeable Ni-Zn battery.

References

(1) Chen, Q. J. Electrochem. Soc. 2014, 161 (10), H643–H646.

(2) Wang C, Chen Q. Chemistry of Materials. 2018, 30 (11), 3894-3900.

Mitigation of Structural and Compositional Instability in 3-Dimensional, Nanoporous Electrocatalysts

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Dealloying has shown increasing utility in the field of electrocatalysis as a tool for the synthesis and development of nanoporous materials possessing high surface-to-volume ratios with controlled morphology and compositional gradient (core-shell structure) [1]. After electrochemical dealloying, the open, bicontinuous, three-dimensional nanoporous nanoparticle electrocatalysts exhibit dramatically enhanced electrocatalytic properties [2,3].

In the development of efficient electrocatalysts for oxygen reduction reaction (ORR), durability is too often ignored in the pursuit of higher activities. For 3-dimensional, nanoporous materials, in addition to the standard mechanisms of electrocatalyst degradation including Pt dissolution/Ostwald ripening and coalescence/aggregation, new modes of morphological and compositional evolution must be considered. Here we use a combination of in-situ and ex-situ experimental techniques to develop insight into the structural and compositional evolution of nanoporous PtNi nanoparticles (np-NiPt) formed through the dealloying of Pt20Ni80 precursor nanoparticles. We demonstrate that surface-diffusion facilitated coarsening, driven by the tendency to reduce the overall surface free energy of the system, is the dominant mechanism of electrochemical active surface area (ECSA) loss, consequently resulting in a decrease in activity [4].

With a better understanding of the interplay between nanoporous structure coarsening and transition metal loss, we have developed strategies to mitigate coarsening and improve operational catalyst stability. The first approach involves the minimization of morphology evolution by impeding step edge movement through the use of foreign adsorbates on the surface. We show that partial monolayer decoration of np-NiPt with Ir, possessing a significantly lower rate of surface diffusion than Pt, acts to pin step edges and results in significant enhancement in catalyst durability as measured by ECSA and ORR activity retention [4]. A second approach uses ionic liquids (IL) strategically placed at the metal/electrolyte interface to limit electrochemically enhanced surface diffusion. Taking advantage of the free volume within the nanoporous nanoparticles and creating a composite catalyst architecture through the incorporation of [MTBD][beti] IL, in addition to the improved oxygen reduction reaction kinetics [2,3], significant improvements in retention of ECSA during accelerated durability testing is observed. The interfacial IL acts to limit the charge dependent formation of a surface metal/electrolyte anion complex which is responsible for the potential dependent enhancement in surface diffusion. With these strategies we will show how more detailed insight into the atomic processes that govern electro-catalytic material instability can begin to break the inverse correlation between activity and durability.

References

1. Snyder, J.; McCue, I.; Livi, K. & Erlebacher, J., J. Am. Chem. Soc. 134, 8633-8645 (2012).
2. Snyder, J.; Fujita, T.; Chen, M. W. & Erlebacher, J., Nature Mater. 9, 904-907 (2010).
3. Snyder, J.; Livi, K. & Erlebacher, J., Adv. Funct. Mater. 23, 5494-5501 (2013).
4. Li, Y.; Hart, J.; Taheri, M. & Snyder, J., ACS Cat. 7(11), 7995-8005 (2017).

Effect and Correction of Ligament Diameter Estimation on Macroscopic Mechanical Properties of Nanoporous Gold

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We developed a computationally efficient and versatile skeleton FEM beam model based on 3D focused ion beam-scanning electron microscope (FIB-SEM) tomography data [1], to bridge computer simulation and experiments. Each ligament is represented by several connected cylindrical beam elements along the skeleton line (ligament path) with different diameters (ligament shape) [2], see Fig.1a. This geometric information is extracted from the tomography data with the plugins "Skeletonize3D" and "Thickness" implemented in the open-source software FIJI.

Comparisons showed a significant overestimation of macroscopic stiffness and strength predicted by the new skeleton FEM beam model [2] in comparison to a solid FEM model of the same tomography [1], see Fig. 1b. Further investigations revealed an overestimation of the diameter values by the "Thickness" algorithm, which are used to generate the beam elements. For a parabolic shaped ligament with 20% diameter variation, a factor of more than two was found in stiffness overestimation [2].

We present several correction approaches for the "Thickness" algorithm that allow tracing back an identified ligament shape to the corresponding true geometry. A direct reconstruction approach (see Fig. 1b-c), a gradient-based optimization approach, and a machine learning approach with neural networks are compared with respect to their reversibility and efficiency. The precision of the approaches was furthermore tested on artificially generated structures, with adjustable geometric information.
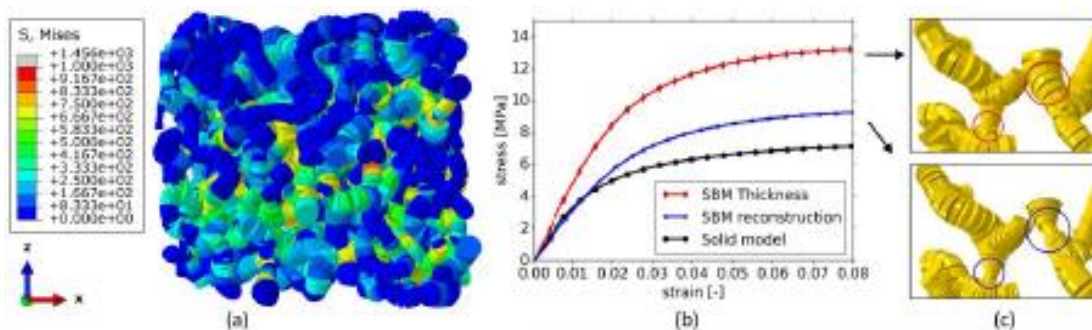

Figure 1. (a) Stress distribution in compressed skeleton FEM beam model (SBM) [2]; (b) macroscopic stress-strain response for solid FEM model [1], SBM with overestimated diameter values derived from "Thickness" algorithm [2], compared to corrected diameter values via reconstruction; (c) cutout volume: the correction of the diameters is visible at ligament neckings.

References

1. K. Hu, M. Ziehmer, K. Wang, E.T. Lilleodden; Philos. Mag. 2016, 96, 3322-3335
2. C. Richert, N. Huber; Metals 2018, 8, 282

Hybrid Materials Made from Nanoporous Metals and Electrically Conductive Polymers as Electro-Chemo-Mechanical Actuators

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Nanoporous metals are suitable as functional materials like sensors or actuators due to its high intrinsic and externally accessible surface area. The surface stress of such materials immersed in electrolyte can be modified by variation of an applied electrical potential [1]. This stress variation is transferred to the underlying bulk atoms, resulting in actuation. The actuation amplitude scales with the ratio of bulk to surface atoms, thus with the intrinsic feature size. Factors like environmental stability and structural coarsening due to surface diffusion restrict the materials choice to noble metals like gold, platinum or palladium [2,3] and are still an issue in terms of performance or long-term stability.

Electrically conductive polymers are another class of electro-chemo-mechanical actuators. Charge balancing leads to the incorporation or removal of co-ions between the polymer chains and results in a volume change [4]. With thin layers of polymer, fast ion exchange is possible, but the stiffness of the underlying substrate limits the effect of actuation.

A combination of both approaches, the coating of the intrinsic surface area of nanoporous metals with electrically conductive polymers, leads to improved electrochemical and actuatoric properties [5].

This contribution presents a manufacturing approach for hybrid materials consisting of nanoporous gold and polypyrrole and focuses on its electrochemical properties as well as on the underlying electro-chemo-mechanical actuation mechanisms. We present different macroscopic specimens with different feature sizes and volume fractions of polypyrrole, their specific capacitance and their strain to charge ratio. In order to get a deeper insight, we explore the microscopic strain-charge coupling of thin planar polypyrrole films and link these results to our nanoporous structures.

References

1. Smetanin, M., Viswanath, et al., J. (2008). Langmuir, 24(16), 8561-8567.
2. Jin, H. J., & Weissmüller, J. (2010). Advanced engineering materials, 12(8), 714-723.
3. Shi, S., Markmann, J., & Weissmüller, J. (2017). Philosophical Magazine, 97(19), 1571-1587.
4. Pei, Q., & Inganäs, O. (1992). The Journal of Physical Chemistry, 96(25), 10507-10514.
5. Wang, K., Stenner, C., & Weissmüller, J. (2017). Sensors and Actuators B: Chemical, 248, 622-629.

Nanoporous Copper-Nickel – Macroscopic bodies of a strong and deformable nanoporous base metal by dealloying

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Owing to their very large surface area to volume ratio, nanoporous metals made by dealloying in aqueous solutions promise significant functionalization. Potential applications arise as actuators, sensors, catalysts or structural materials with tunable mechanical properties. An obvious requirement for a materials competitive ability in these fields is affordability. In addition, deformability is required to avoid premature failure upon exposure to stress concentrations or to designed mechanical load. So far, macroscopic samples of nanoporous metals with a high surface area and deformability have been limited to precious, and thereby costly, metals such as Au, Pd and Pt.

Here we present nanoporous Copper-Nickel (npCN), a nanoporous base metal that can be made in macroscopic dimensions (≥ several mm in size) and shows significant deformability. Fabricated through dealloying in aqueous media, npCN exhibits a uniform, bicontinous network structure with feature sizes that can be controlled from 13 to 40 nm through thermal annealing. Continuous com-pression tests find ductile deformation behavior accompanied with a high strength compared to other nanoporous base metals as well as macroporous Cu- and Ni-foams with similar solid fraction.

References

1. L. Lührs, J. Weissmüller, Scripta Materialia 155 (2018) 119–123

Role of grain boundary in plastic deformation of nanoporous gold

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The population of grain boundaries is one of the major differences between a nanoporous (np) metal prepared by dealloying and a compact of metal nanoparticle. The np metal can gain a grain size that is orders of magnitude larger than the pore size,[1] while the grain size and pore size are often comparable in compacted nanoparticles. Most previous studies on the mechanical properties of np metals have been focusing on samples with larger grain sizes, such as the np Au dealloyed from Au-Ag alloys, where the grain boundary area is negligible compared with the surface area1. Some recent studies[2] revealed that the deformation behavior of the nanocrystalline nanoporous metals differs from those with minimal grain boundaries, indicating that the grain boundary may play critical role in deformation of np metals. Here we present a study on the compression behavior of mm-sized nanoporous gold samples, with identical pore sizes but different grain sizes. The aim is to identify the role of grain boundary in the plastic deformation of nanoporous gold, and the contribution of grain boundary to the strength of nanoporous gold. The roles of the grain boundaries were characterized by comparing the ligament strengths (corrected using a method presented in Refs. [3-5]) and the surface effect on the strength (see the method in Refs. [7-8]) in samples with different grain sizes.

References

1. H.-J. Jin, L. Kurmanaeva, J. Schmauch, H. Rosner, Y. Ivanisenko, J. Weissmüller, Deforming nanoporous metal: Role of lattice coherency, Acta Mater. 57 (2009) 2665–2672.

2. E.J. Gwak, H. Jeon, E. Song, N.R. Kang, J.Y Kim, Twinned nanoporous gold with enhanced tensile strength, Acta Mater. 155 (2018) 253-261.

3. L.-Z. Liu, X.-L. Ye, H.-J. Jin, Interpreting anomalous low-strength and low-stiffness of nanoporous gold: Quantification of network connectivity, Acta Mater. 118 (2016) 77–87.

4. L.-Z. Liu, H. J. Jin, Scaling equation for the elastic modulus of nanoporous gold with fixed network connectivity , Appl. Phys. Lett. 110 (2017) 21.

5. H.-J. Jin, J. Weissmüller, D. Farkas, Mechanical response of nanoporous metals: A story of size, surface stress, and severed struts, MRS Bull. 43 (2018) 35–42.

6. H.J. Jin, J. Weissmüller, A Material with Electrically Tunable Strength and Flow Stress, Science. 332 (2011) 1179–1182.

7. P. Wu, X.-L. Ye, H.-J. Jin, Monolayer oxide enhanced flow stress in nanoporous gold: the size dependence, Mater. Res. Lett. 6 (2018) 508–514.

Electrowetting at Nanoporous Surfaces: Switchable Droplet Shape, Spreading and Imbibition

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Electrically conductive substrates, such as surfaces of nanoporous metals or semiconductors, allow one to control the wetting energies of electrolytes by electrical potentials. Thereby, it is possible to tune droplet shape and liquid spreading dynamics at surfaces. However also the imbibition into the porous surface is under external control via electrical potential-dependent curvatures of the liquid menisci within the nanopores, see Fig. 1. Here we present experiments with aqueous electrolytes on static droplet shapes, on spreading at, and capillarity-driven spontaneous imbibition into, nanoporous gold, copper-nickel and silicon monoliths.

Our findings demonstrate that the high electric conductivity along with the pathways for fluid/ionic transport render the nowadays readily available nanoporous metals particularly suitable for the study of (electro-) wetting phenomena at nanostructured surfaces with potential applications as electrocapillary pumps, flow sensors, and switchable fluid-in-fused surfaces.

Figure 1. (upper panel) Transformation of a sessile aqueous electrolyte droplet on nanoporous silicon from the non-wetting Cassie-Baxter to the partial-wetting Wenzel state under external electrical potential control. (lower panel) Schematics of spontaneous electrolyte imbibition in a tubular capillary and in nanoporous gold under electrical potential control.

References

Y. Xue, J. Markmann, H. Duan, J. Weissmüller, and P. Huber: Switchable Imbibition in Nanoporous Gold, Nature Communications 5, 4237 (2014).

L. Lührs and J. Weissmüller: Nanoporous Copper-Nickel–Macroscopic bodies of a strong and deforma-ble nanoporous base metal by dealloying, Scripta Materialia 155, 119 (2018).

Verifying Larché-Cahn theory by measuring open-system elasticity of nanoporous palladium(-gold)-hydrogen

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Monolithic nanoporous metals with large surface-to-volume ratio are suitable for studying the mechanical behavior of nanostructured metals via conventional, macroscale mechanical testing approaches. Nanoporous gold is usually the model system of choice. Most recently, we established the synthesis of monolithic and uniform bodies of nanoporous palladium (np Pd) as an alternative and explored the mechanical responses of this material through electrochemically controlled hydrogen sorption [1-3]. Here, we report the synthesis of monolithic nanoporous palladium and palladium-gold (Pd-Au) samples by electrochemically dealloying Cu85Pd15 and Cu85Pd12.5Au2.5, respectively. Both nanoporous materials show ligament sizes below 10nm, which allow fast hydrogen diffusion or redistribution across their diameter when stress gradients are induced by bending. The Young's modulus variation of np Pd and Pd-Au during hydrogen absorption/desorption are measured by a dynamic mechanical analyzer. It is found that hydrogen sorption induced more than 30% reversible compliance variation in np Pd, suggesting new opportunities in the design of functional materials with switchable elastic stiffness. Moreover, experimentally measured elastic coefficients of H-diluted np Pd(-Au)-H single-phases show excellent agreement with the prediction by the Larché-Cahn theory of open-system elasticity. Our experiments provide the first direct verification of the Larché-Cahn theory as a mile-stone of 20th-century thermodynamics.

References

1. S Shi, J Markmann, J Weissmüller. Actuation by hydrogen electrosorption in hierarchical nanoporous palladium. Philosophical Magazine 97 (2017) 1571-1587.
2. S Shi, J Markmann, J Weissmüller. Synthesis of uniform bulk nanoporous palladium with tunable structure. Electrochimica Acta 285 (2018) 60-69.
3. S Shi, J Markmann, J Weissmüller. Verifying Larché–Cahn elasticity, a milestone of 20th-century thermodynamics. Proceedings of the National Academy of Sciences 115 (2018) 10914-10919.

Connections between Topology and Macroscopic Mechanical Properties of Three-Dimensional Open-Pore Materials

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This work addresses a number of fundamental questions regarding the topological description of materials characterized by a highly porous three-dimensional structure with bending as the major deformation mechanism. This is the dominant deformation mechanism in nanoporous gold. Highly efficient finite-element beam models were used for generating data on the mechanical behavior of structures with different topologies, ranging from highly coordinated bcc to Gibson–Ashby structures, see Fig. 1(a). Random cutting enabled a continuous modification of average coordination numbers ranging from the maximum connectivity to the percolation-cluster transition of the 3D network. Via data mining, the interdependencies of topological parameters and relationships between topological parameters with mechanical properties were discovered.

The average coordination number z serves as a common key for determining the cut fraction, the scaled genus density, and the macroscopic mechanical properties. The dependencies of macroscopic Young's modulus, yield strength, and Poisson's ratio on the cut fraction (or average coordination number) could be represented as master curves, covering a large range of structures from a coordination number of 8 (bcc reference) to 1.5, close to the percolation-cluster transition, see Fig. 1(b). It was found that all data for macroscopic Young's modulus and yield strength are covered by a single master curve. This leads to the important conclusion that the relative loss of macroscopic strength due to pinching-off of ligaments corresponds to that of macroscopic Young's modulus. Experimental data in literature support this unexpected finding.
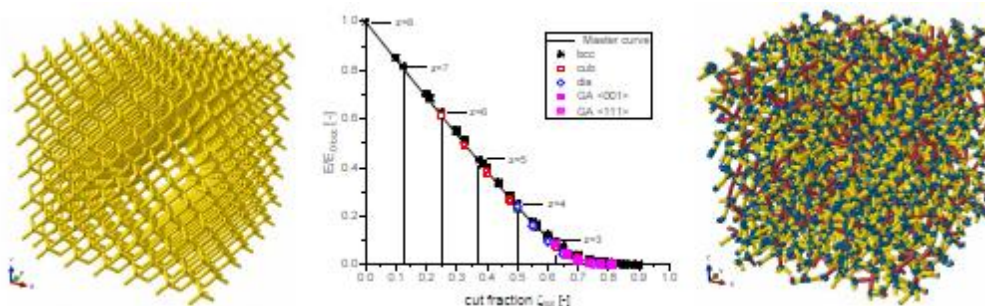

Figure 1. (a) FEM beam model for diamond structure with coordination z=4, (b) Master curve for Young's modulus incorpo-rating all investigated structures; (c) FEM model for validation of the derived structure-property relationships.

References

N. Huber, Frontiers in Materials, Computational Materials Science, accepted (2018)

Kinetics of vapor phase dealloying

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Vapor phase dealloying is a new method to fabricate porous materials by using vapor pressure difference of constituent elements. However, less information is available about fundamental studies for the kinetics of this dealloying process. In this work, based on the investigation for the effect of dealloying parameters such as dealloying time, dealloying temperature and dealloying vacuum on porous structure, the systematical analysis of the kinetics for porous structure formation during vapor phase dealloying has been presented by using the Cu-Zn alloy as the model system. Results demonstrate that in the process of vapor phase dealloying, the generated intermediate phase is the premise for the porous structure formation and the kinetics of porous dealloying is controlled by the interface.

Micro-mechanical behavior of nanoporous gold with and without an electrochemical environment

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The effect of the size ratio of pillar diameter to average ligament diameter on the electro-chemo-mechanical coupling of nanoporous gold (NPG) was investigated by in situ micro-compression in an electrochemical cell. Micro-pillars of NPG with varying size ratios were produced by focused ion beam (FIB) milling, and then mechanically tested with and without immersion in an electrolyte using a nanoindenter equipped with a flat punch. A critical size ratio was determined at which the test structure can be considered a representative volume of material resulting in uniform deformation and reproducible stress-strain behavior. Using a novel loading profile, the contribution to the dis-placement due to the actuation could be decoupled from the compression-induced deformation. Electro-chemo-mechanical coupling measurements showed that the strength of pillars increased considerably when surface adsorption occurred, i.e. under positive applied potential, and the stress response to potential jumps was found to be fast and reversible.

Oxide-related performance improvement of nanoporous gold electrodes for electrochemical CO2 reduction
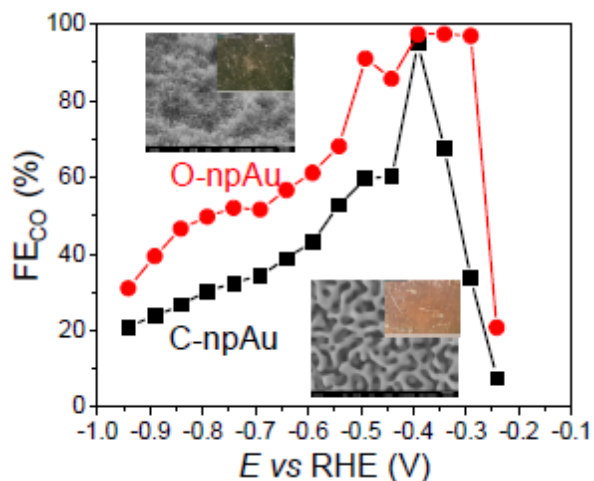
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Tremendous efforts have been devoted to substitute traditional energy, which mostly originates from fossil fuels, with renewable energy including wind, solar and hydraulic sources. The direct consequence of using fossil fuels is the accumulation of atmospheric CO2, which is a notorious greenhouse gas, ever since industrialization. CO2 contributes to global warming and extreme weather conditions. Closing the anthropologic cycle of CO2 is one of the feasible ways to remove CO2 and utilize CO2 in a manner that we consume our energy today.

In this work we demonstrate that nanoporous gold covered with a thin oxide layer shows an extremely low overpotential for CO2 to CO reduction. To evaluate the effect of the Au surface oxide on CO2 reduction we used a clean nanoporous gold sample as reference. Our results suggest that the origin of the enhanced performance of oxide covered nanoporous gold is due to a combination of the presence of the Au oxide layer and a high density of defects. The presence of the Au oxide has a two-fold benefit: a) it reduces the overpotential for the CO2 to CO reaction and b) it suppresses the hydrogen evolution.

Mechanical properties of nanoporous gold – A comparative investigation on the impact of the composition of the master alloy

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Due to its chemical stability and the tunable structure size from a few to several hundred nanometers, nanoporous gold (NPG) is an attractive model system for small-scale material behavior. In this sense, its mechanical properties have been investigated over many years. Clear distinctions in stiff-ness and strength caused by variations of the solid fraction, φ, have been reported. Yet, a systematic investigation is still missing. Due to different processing approaches, the comparability of the published data is restricted. Specifically, the role of the initial composition of precursor alloys (which control φ) and of the processing steps call for a systematic study.

Here, we systematically varied the initial alloy composition and the dealloying procedure of NPG. We investigated the mechanical response, emphasizing comparability. AuAg alloys with gold amounts between 20 and 35 at.% were dealloyed electrochemically in 1M $HClO_4$ or via free corrosion in concentrated HNO_3. Compression tests with continuous loading and with load/ unload protocols explored the stress-strain behavior, Young´s modulus and Poisson´s ratio. We confirm that the mechanical response varies significantly depending on the master alloy compositions. This provided a database for the variation of the mechanical response with solid fraction for given ligament size. The poster will present the results and discuss them in the context of current approaches to strength and stiffness of nanoscale metal network structures.

Operando TEM Investigation of Lithium Storage Mechanisms in Nanoporous Alloy-Type Lithium-Ion Anodes

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High-capacity alloy-type lithium-ion battery anodes undergo large volume changes (~300%) during lithiation.1 The resulting stresses can cause pulverization and delamination of active material from the current collector, rendering it electrochemically inaccessible. Previous work demonstrated that nanoporous electrode materials, consisting of bicontinuous network of nanoscale solid ligaments and pores, have improved cycling performance compared to their bulk counterparts. Currently, it is hypothesized that this volume change is minimized due to a buffering mechanism in which the ligaments expand while the pores shrink, resulting in a smaller lithiation-induced net volume change.[1] In an attempt to verify this hypothesis, Detsi and his colleagues have used synchrotron-based transmission X-ray microscopy (TXM) to image these volume changes and found that nanoporous Sn grains accommodate the lithiation-induced volume changes better than dense Sn.[2] However, the TXM is only able to probe the volume change in sub-micrometer sized Sn grains. In order to confirm the above hypothesis, one needs to observe the structural evolution of the nanoscale pore-ligament structure of 3D nanoporous alloy-type Li-ion battery anodes during galvanostatic cycling. This will be accomplished through the use of transmission electron microscopy (TEM). A Hummingbird Scientific electrochemistry TEM specimen holder will be used to facilitate the lithiation and delithiation of a "nanobattery[3]" while different TEM techniques are performed simultaneously. We have used the focused ion beam to create dealloyed nanoporous metals anodes as seen in Figure 1. Through this methodology, this experiment will be able to address fundamental questions involving structural changes in nanoporous alloy-type lithium-ion battery anodes during lithiation / delithiation cycles.
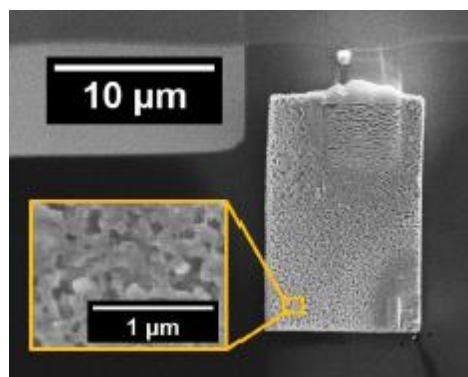

Figure 1. Nanoporous metal electrode fabricated using the fo-cused ion beam for use in an operando TEM "nanobattery"

References

1. Cho, J. Porous Si anode materials for lithium rechargeable batteries. J. Mater. Chem. 20, 4009 (2010).
2. Cook, J. B. et al. Nanoporous Tin with a Granular Hierarchical Ligament Morphology as a Highly Stable Li-Ion Battery Anode. ACS Appl. Mater. Interfaces 9, 293–303 (2017).
3. Gu, M. et al. Demonstration of an electrochemical liquid cell for operando transmission electron microscopy observation of the lithiation/delithiation behavior of Si nanowire battery anodes. Nano Lett. 13, 6106–6112 (2013).

Computational and Experimental Observation Of Crack Propagation in Nanoporous Gold

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We present a combined experimental and simulation-based study examining crack propagation in nanoporous gold. Thin film samples prepared via chemical dealloying are deformed in situ in tension under a constant strain rate until fracture, and are analyzed with TEM. Molecular dynamics simulations are conducted on a computationally generated, morphologically similar sample to observe and understand the specific fracture mechanisms in detail. The resulting mechanical properties of both computational and experimental samples are examined and compared. These experiments provide new and surprising insight into the mechanical response of NPG – specifically, observing rare examples of brittle fracture in individual ligaments and strain hardening.

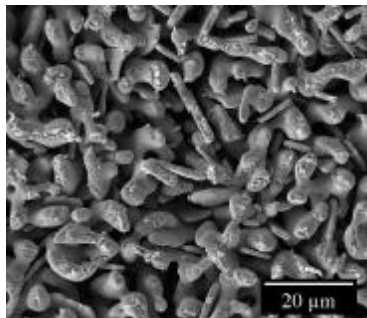# Novel Electronic Applications of Porous Niobium

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Liquid metal dealloying (LMD) is an emerging processing technique to form bicontinuous structures of micron-scale metal ligaments and pores by selectively dissolving one component of an initially homogeneous alloy in a metallic melt. The three-dimensional connectivity of the porous structures formed by LMD are promising in a variety of applications.

High performance tantalum capacitors are a ubiquitous part of modern electronic infrastructure widely employed in aerospace and military applications. Niobium is a promising alternative to tantalum in this market, providing many of the same advantageous properties at a lower cost and with greater natural abundance. We show that LMD niobium can be used to fabricate simple, scalable capacitors with high mass-specific capacitance.

As niobium is one of only two naturally-occurring metal type-II superconductors, LMD niobium also offers us the opportunity to observe size effects within these materials, which possess a unique combination of structural and intrinsic electronic properties. We are studying the superconducting transition of porous niobium at a range of length scales, thus gaining insight into the behavior of type-II superconductors. These bulk porous samples can also be used to create composite materials with uniform interface densities throughout the material. LMD niobium can be readily coated or filled with other materials of interest, allowing us to study superconducting interfacial effects in the bulk that have previously only been observed in thin films and nanostructures.

Electrochemical properties of three-dimensional bicontinuous porous carbon produced by liquid metal dealloying

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Lithium-ion batteries (LIBs) have been widely used as power sources due to high energy density, thermal and chemical stability, and low cost, since, it had been commercialized in the early 1990s. Commercial LIBs use graphite as an anode active material, but higher-capacity & faster-lithiation electrode materials are highly desirable for more demanding applications which facilitate our daily life. Consequently, there have been intensive studies for the next-generation LIBs to overcome the rate limit of current LIBs [1]. Graphene, hard carbon, carbon nanotube, and carbon composite materials have been considered as candidates due to their high rate-capability with superior reversible capacity even higher than the theoretical capacity of graphite. However, these newly suggested active materials disregard the importance of anode potential which is essential for practical battery. Their outstanding capacity is due to the additional redox behavior on the surface which is distinct from intercalation/de-intercalation redox system on interlayers of graphite. Consequently, a flat plateau of potential in charge-discharge behavior disappears. The lack of flat plateau indicates uncertain operating voltage of cell, thus these carbon materials are superior for capacitor but not for battery [2].

In this study, the electrochemical properties of three-dimensional bicontinuous porous carbon (3Dbp-carbon) produced by liquid metal dealloying were systematically investigated. 3Dbp-carbon demonstrated the large specific surface area with the comparable crystallinity, and the high rate-capability with a maintained flat plateau was observed in charge-discharge behavior. In addition, the effect of following activation and graphitization processes were studied based on the microstructural changes and its relationship with battery properties.

References

1. Y.S. Hu, P. Adelhelm, et al., Adv. Funct. Mater. 17 (2007) 1873-1878.
2. A. Eftekhari, Energy Storage Materials, 7 (2017) 157-180.

Creation of Nanoporous Carbon and Silicon Structures Through Liquid Metal Dealloying of Mn80Si10C10

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Creation of nanoporous silicon and carbon structures has the potential to advance energy storage technology as both porous silicon and carbon are excellent candidate materials for Li-ion battery electrodes. My efforts have focused on liquid metal dealloying of the Mn80Si10C10 system in Bi with the goal of etching the Mn/Bi phase in HNO3 to realize a nanoporous structure of either C or Si. So far successful dealloying of Mn80Si10C10 ingots has been achieved, however, treatment with HNO3 caused the sample to fall apart. The Mn80Si10C10 system shows promise in yielding fully porous silicon and carbon structures via liquid metal dealloying in Bi.

Microstructural Characterization Using Two-Point Statistics: Applications to Nanoporous Gold

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Nanoporous gold is a bicontinuous structure with a network of pores and ligaments (Figure 1a), whose size sets optical, chemical and mechanical properties of the material [1]. The microstructural length scales, interfacial curvatures, and their spatial distributions can be quantified using a novel two-point statistics method introduced by Sun. et al [2]. This extends upon two-point statistics methods that only provide information about the correlation between quantities in the bulk of the micro-structure to also include interfacial quantities. Coarsening of a bicontinuous microstructure following spinodal decomposition with interfacial evolution controlled by bulk diffusion is studied using phase field modeling [3]. Two-point Pearson auto-correlations of mean curvature (H) and the binary order parameter (Phase) are calculated providing information about characteristic length scales in the structure. A plot of the radially averaged two-point Pearson auto-correlations is shown in Figure 1b. The auto-correlations show regions of correlation and anti-correlation between the phases, with a large region of anti-correlation in the H auto-correlation. The peaks in this plot give the characteristic length scales in the structure. The bulk diffusion results are compared to a surface diffusion-governed phase field model, as well as experimental studies of bicontinuous nanoporous gold found during coarsening [4,5]. The similarities and differences between the datasets, as well as insights into the mechanisms of nanoporous gold coarsening are discussed.
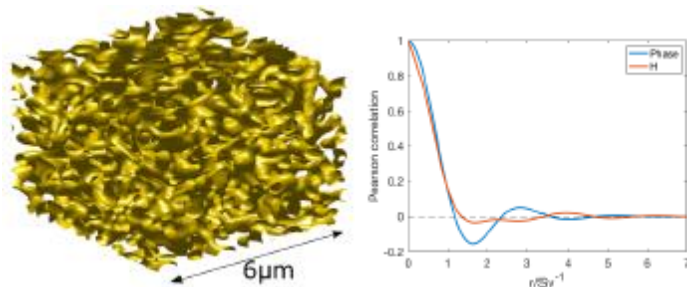

Figure 1. (a) Nanoporus gold microstructure; (b) radially averaged two-point Pearson auto-correlation of the binary order parameter (Phase) and interfacial mean curvature (H)

References

[1] Chen-Wiegart, Y. et al. Structural evolution of nanoporous gold during thermal coarsening. Acta Mater. 60, 4972-4981 (2012).

[2] Sun, Y. et al. Analytics on large microstructure datasets using two-point spatial correlations: Coarsening of dendritic structures. Acta Mater. 132, 374-388 (2017).

[3] Sun, Y. Spatio-Temporal Analysis of Coarsening in Complex Structures Using Two-Point Statistics. Ph.D. Thesis. (2018).

[4] Hu, K. et al. Nanoporous gold: 3D structural analyses of representative volumes and their implications on scaling relations of mechanical behavior. Philos Mag. 96, 3322-3335 (2016).

[5] Ziehmer, M. et al. A principal curvatures analysis of the isothermal evolution of nanoporous gold: Quantifying the characteristic length scales. Acta Mater. 120, 24-31 (2016).

Understanding dioxygen activation on nanoporous gold. A DFT and microkinetic modeling study

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Nanoporous gold (np-Au) is a catalytically highly active material, prepared by selectively dealloying silver from a gold-silver alloy. It can promote aerobic CO oxidation and a range of other oxidation reactions. It has been de-bated whether the remarkable catalytic properties of np-Au are mainly due to its structural features or whether the residual Ag remaining in the material after dealloying is decisive for the reactivity, especially for the activation of O2. Recent theoretical studies provided evidence that Ag impurities can

Figure 1. A catalytic cycle for O_2 splitting to atomic O by water.

facilitate the adsorption and dissociation of O2 on np-Au. Yet, these studies predicted quite a high activation barrier for O2 dissociation on Au-Ag alloy catalysts, whereas experimentally reported activation energies are much lower. In this work we present alternative routes for O2 activation via its direct reaction with CO or H2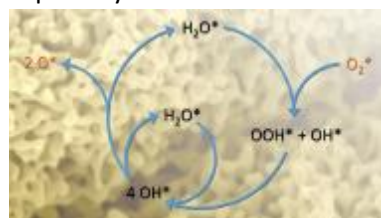O on nanoporous gold modeled by the stepped Au(321) surface with Ag impurities on the basis of DFT calculations. In all of the reactions considered, surface atomic O is generated via a sequence of elementary steps with calculated low activation energies of < 0.4 eV with respect to co-adsorbed reactants.

We have applied microkinetic modeling to study the mechanism of CO oxidation and the influence of water in the reaction mixture on the kinetics. Surprisingly, we find that, despite low activation energies, the water-catalyzed route has a very low TOF and does not increase the overall reaction rate. In contrast, the direct reaction between CO and O2 is the main reaction channel on pure Au and Au with Ag impurities. Ag impurities are shown to increase the adsorption strength of O2, which leads to a higher TOF.
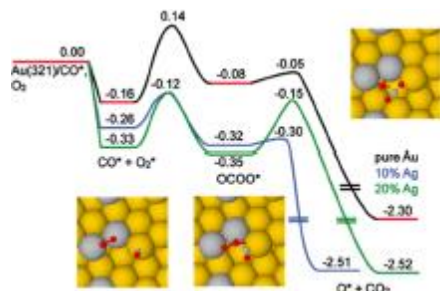

Figure 2. A direct reaction between CO and O_2 forming CO_2 and atomic O on Au(321) with and without Ag impurities.

Nanoporosity Evolution Derived from Metal Dissolution Rates

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The emerging transition from an oil-energy based society to an electrical-energy one relies on development of electrochemical energy conversion and storage systems that are active, stable, selective, safe and cost effective. Many of these properties can be tuned when employing materials at the nanoscale dimension. Despite many different synthesis routes to grow nanoparticles of almost any material and composition, with well-defined size distribution, morphology, and surface properties, the same is not true when creating nanoscale features from dealloying processes. The firm established view on nanoporosity evolution by dealloying of a bimetallic alloy, having its components far apart in the electrochemical series, relies on dissolution (corrosion) of the least noble component, and surface diffusion against a negative gradient of the nobler component. While the success of this mechanism is undeniable in simulating the same length scale features found in real-world de-alloyed examples such as nanoporous gold, exotic systems such as IrOs alloys tend to form nanoporosity with rather larger pore sizes than expected from surface diffusion considerations. Our work, then, is directed to explain pore size discrepancies using IrOs alloys as an example by using in situ experimental monitoring of the dissolution processes taking place during electrochemical dealloying, observing both elements in the alloy. By varying the initial composition of the IrOs alloy, we were able to observe a correlation between pore size and dissolution rates, key to optimize the alloy properties to be an active, stable and conductive catalyst for the oxygen evolution reaction in acidic media. We further explore this alternative pathway to evaluate its impact on nanoporous evolution on other bimetallic alloy systems that may have practical applications in fuel cells, electrolyzers and battery technologies.

Bi-continuous Pattern Formation in Thin Films via Solid-State Interfacial Dealloying

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Solid-State Interfacial Dealloying (SSID), as an emerging method for fabricating interconnected bi-continuous and high surface porous metal at nano/meso scale, will enable design a wide range of functional materials for applications such as sensing, energy storage and catalysis. However, the detailed mechanism for the pattern formation remains unclear, especially regarding the complex morphology at the dealloying front. To better understand the SSID process, we prepared Fe-Ni/Mg film samples by Direct-Current sputtering and Rapid Thermal Processing to introduce dealloying to form Fe/Mg-Ni bi-continuous structure. The phase separation and other phenomena which occur simultaneously, leading to the ligament formation, were analyzed. The morphology of the materials evolved from SSID, as well as the elemental distribution within the structure, were characterized using a combination of X-ray imaging and electron microscopy methods. The results shed the light on the underlying mechanism of the SSID, for enabling future materials design using the new process.
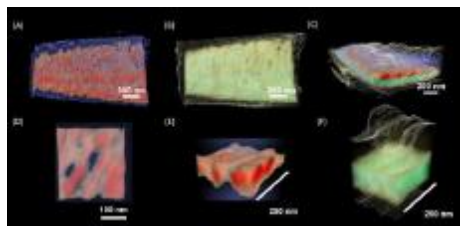
Figure 1. 3D fluorescence tomography of Fe50Ni50 thin film dealloyed with Mg at 460oC for 30 min. Separate Fe (A) and Ni (B) X-ray fluorescence (XRF) tomography, overlay of Fe and Ni (C). The sub-volumes from XRF tomography are shown in (D)-(F), with top view of Fe (E), side view of Fe (F) and Ni (G).

Nanoporous Aluminum Two Ways

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Nanoporous metals are predominantly produced by selective dissolution of the less noble element in an alloy, while simultaneously allowing the more noble element to re-arrange to form a bicontinuous network of interconnected ligaments. However, it is limited by only permitting the formation of these structures from the more noble element in a binary alloy. A similar bicontinuous morphology is observed from the phase-separation process of a solid solution via spinodal decomposition. Once the binary alloy is decomposed, the more noble element can be removed chemically or electrochemically. Here, we demonstrate this processing technique with bulk Al40Zn60, comparing the structure of the spinodally decomposed material to the structure of nanoporous aluminum made by liquid metal dealloying (LMD) of the same alloy in bismuth. Each case produces an interconnected and bicontinuous network of aluminum, with a length scale dependent upon the parameters of the phase-separation process. We determined there is a direct correlation between the duration of the Al-Zn decomposition to the aluminum ligament size.

Dynamical Insights to Nanoporous Structure Evolution during Electrochemical Dealloying Provided by In-Situ Resistometry

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Simultaneous monitoring of charge flow and electrical resistance increase proves to be an ideal combination for analyzing the etching progress during electrochemical dealloying. Exemplarily, a detailed analysis of the formation of nanoporous gold, platinum and palladium is given here, providing deeper insights to the process. Due to porosity evolution and concomitant oxide formation, the electrical resistance of the materials increases by three orders of magnitude during selective etching, which in accordance with ex-situ studies can be demonstrated to occur in two steps referred to as 'primary (or bulk) dealloying' and 'secondary (or ligament) dealloying [1].

In the present contribution, a model is presented [2], which describes the resistance increase during etching as governed by the reduction of the master alloy backbone in favor of the nanoporous struc-ture. This approach allows an evaluation of the etching front propagation (primary dealloying) as well as the status of the already porous structure (secondary dealloying). A comparison of the data obtained for different sample metals shows that secondary dealloying is pronounced strongest for nanoporous gold. This behaviour is assigned to the ligament sizes in the respective structures, which are known to scale inversely with the melting points.

References

[1] X.-L. Ye et al., J. Electrochem. Soc 161, C517 (2014)

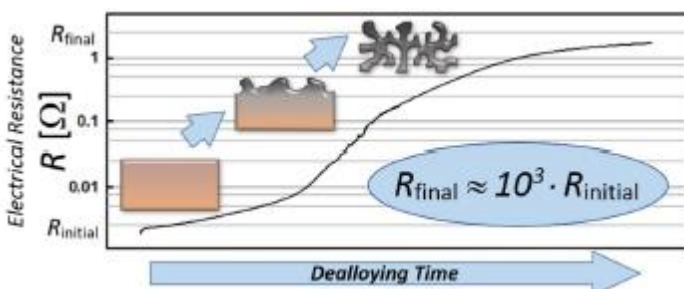[2] E. Steyskal et al., Phys. Chem. Chem. Phys. 19, 29880 (2017)

Figure 1. Resistance increase by three orders of magnitude during dealloying an Ag-Au alloy. Image taken from: E. Steyskal et al., Phys. Chem. Chem. Phys. 19, 29880 (2017) http://dx.doi.org/10.1039/C7CP05706G

Visualizing under-coordinated surface atoms on three dimensional nanoporous gold catalysts

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Under-coordinated atoms at surface steps and kinks play a vital role in the catalytic activities of nanostructured catalysts that usually possess a three-dimensional (3D) complex morphology. Atomic-scale characterization of the surface defects on 3D catalysts is crucial to understand the underlying catalytic mechanisms, particularly gold catalysis that has been debated for decades. Here we report quantitative measurements of the intricate 3D geometric shape and surface atomic structure of nanoporous gold (NPG) catalysts. Real-space 3D atomic configurations illustrate geometrically necessary surface defects (GNSDs) on the curved surfaces of NPG and reveal the intrinsic correlation between the GNSD density and catalytic activities, which offers atomic insights into the catalysis of NPG.
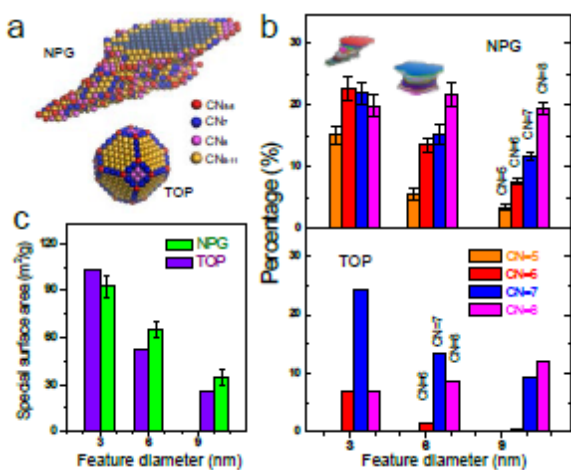
Figure 1. Quantitative measurements of under-coordinated surface atoms of NPG.

References

1. Liu, P., et al. Adv. Mater. 2016, 28, 1753-1759.
2. Fujita, T., et al. Nature Mater. 2012, 11, 775-780.

Three-dimensional bicontinuous nanoporous materials by vapor phase dealloying

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Three-dimensional bicontinuous open (3DBO) nanoporosity has been recognized as an important nanoarchitecture for catalysis, sensing, and energy storage. Dealloying, i.e., selectively removing a component from an alloy, is an efficient way to fabricate nanoporous materials. However, electrochemical and liquid-metal dealloying methods can only be applied to a limited number of alloys and usually require an etching process with chemical wastes. Here, we developed a vapor-phase dealloying (VPD) method by utilizing the vapor pressure difference between solid elements to selectively evaporate a component from an alloy. This method can be applied to a variety of elements from less-noble metals to inorganic elements regardless of their chemical, and electrochemical activity and electric conductivity. The elements with low melting point can also be fabricated using a low dealloying temperature by reducing dealloying pressures. By using Zn–Co as a prototype system, we demonstrated that 3DBO nanoporosity of Co can be achieved by VPD and the pore size can be tailored to a wide size range from tens of nanometers to micrometers by controlling dealloying temperature, time and pressure. In particular, the dealloying pressure significantly changes the rate-limiting dealloying mechanisms from a low-vacuum bulk diffusion controlled process to a high-vacuum surface diffusion controlled process. Importantly, the sublimated elements can be fully recovered and do not cause any environmental issues. This environmentally friendly and highly efficient dealloying method paves a new way to fabricate and design bicontinuous nanoporous materials for a wide range of structural and functional applications.