

# Emerging Science and National Priorities in Metals and Metallic Nanostructures

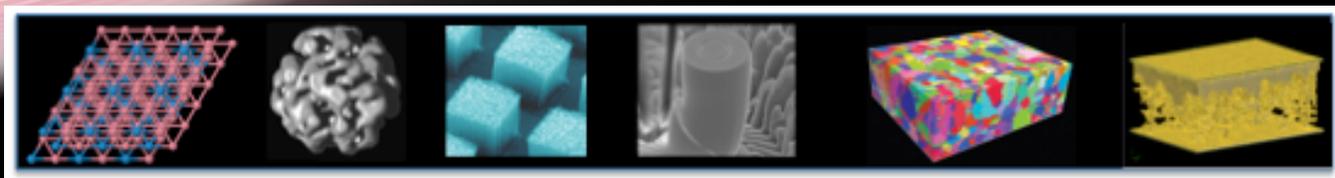
*Report on the NSF Sponsored Workshop*

*June 13 – 14, 2012*

*Held at the University*

*Of California*

*Santa Barbara*



## 1. Executive Summary

In the next decade, fundamental research in metals and metallic nanostructures (MMN) has the potential to continue to transform science into innovative materials, devices, and systems. A workshop to identify emerging and potentially transformative research areas in MMN was held on June 13 and 14<sup>th</sup>, 2012 at the University of California Santa Barbara. There were 47 attendees at the workshop, representing a broad range of academic institutions, industry and government laboratories.

The MMN workshop aimed to (i) identify significant research trends, scientific fundamentals and recent breakthroughs that enable new or enhanced MMN performance, either alone or in a more complex materials system for a wide range of applications; (ii) assess the role MMN can have in R&D areas of high national priority, such as the Materials Genome Initiative, the National Nanotechnology Initiative, the Advanced Manufacturing Initiative, STEM education and workforce development, and innovative, cyberinfrastructure for materials science research and education; (iii) Examine international research in MMN, assess the position of the United States relative to the field, worldwide, and recommend mechanisms to ensure US leadership in this field; (iv) evaluate the NSF funding mechanisms relative to these opportunities and challenges.

A central theme of the Workshop was the view that research in metals and metallic nanostructures has provided and will continue to provide benefit to the nation through the coupling of experiment, theory, and simulation to link atomistic, nanoscale, microscale, and mesoscale phenomena at time scales for an ever widening range of applications. Within this overarching theme, the workshop participants identified emerging research opportunities that are categorized in terms of:

- 3-D and 4-D Materials Science
- Structure Evolution and the Challenge of Heterogeneous and Multicomponent Systems
- The Science Base for Property Prediction Across the Lengthscales
- Nanoscale Phenomena at Surfaces – Experiment, Theory, Simulation
- Prediction and Control of the Morphology, Microstructure, and Properties of “Bulk” Nanostructured Metals
- Functionality and Control of Materials Far from Equilibrium
- Hybrid and Multifunctional Materials Assemblies
- Materials Discovery and Design - Enhancing the Theory – Simulation - Experiment Loop

The workshop also addressed critical issues limiting the U.S. Materials Research Infrastructure as well as Global Competitiveness, Education and Workforce Development.

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**Tuesday, June 12th**

5:00-8:00PM	Kick Off BBQ	Goleta Beach, 'D'
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**Wednesday, June 13th**

7:00-7:45AM	Workshop Check-In and Continental Breakfast	ESB 1001
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7:45-8:00AM	Welcome and Charge to the Workshop Participants	Eric Taleff & Tresa Pollock
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8:00-9:15AM	Setting the Stage: Grand Challenges and the Role of Metals and Metallic Nanostructures	
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8:00-8:15AM	Nanostructures in Biomedical Applications and Environment Stewardship	Ken Vecchio
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8:15-8:30AM	Energy and Environment	Jonah Erlebacher
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8:30-8:45AM	Propulsion and Transport	Tresa Pollock
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8:45-9:00AM	Manufacturing	John Allison
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9:00-9:15AM	Information	Richard LeSar
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9:15-10:00AM	Panel 1: Broad Perspectives on Grand Challenges: Industry, Government Laboratories, International	*Liz Holm, Don Shih, Sung Kang, Harry Kington, Peter Gumbsch
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10:00-10:30AM	Coffee Break	ESB 1001
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10:30-12:00PM	Research Challenges and Opportunities Materials Discovery and Design: Coupling Computation with Experiment	
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10:30-11:00AM	Atomic Scale	Anton Van der Ven & Emmanuelle Marquis
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11:00-11:30AM	Nanoscale	Vidvuds Ozolins & Dan Gianola
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11:30-12:00PM	Mesoscale	Surya Kalidindi & Rusty Gray
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12:00-1:00PM	Lunch	ESB 1001
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1:00-2:30PM	Research Challenges and Opportunities	
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1:00-1:30PM	The Challenge of Multicomponent Systems: Atomistics, Thermodynamics and Kinetics	Dallas Trinkle & Peter Voorhees
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1:30-2:00PM	Quantification and Prediction of Structure across the Lengthscales	Nik Chawla & Mike Mills
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2:00-2:30PM	Prediction of Properties and Performance: Top Down vs. Bottom Up	Dennis Dimiduk & Peter Gumbsch
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2:30-3:00PM	Coffee Break	ESB 1001
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3:00-4:00PM	Research Challenges and Opportunities Cont'd	
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3:00-3:30PM	New Enabling Synthesis Paths for Structural and Functional Metallics	Boyd Mueller & Chris Schuh
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3:30-4:00PM	Metallic Materials in Extreme Environments	Bob Odette & Easo George
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4:00-4:15PM	Summary and Assembly of Break-out Sessions	
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4:15-5:15PM	Break-outs on Basic Science Challenges	
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5:15-5:30PM	Wrap-up and Preparation for Day 2	
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6:00-8:30PM	Reception and Dinner	Faculty Club Courtyard
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**Thursday, June 14th**

7:00-8:00AM	Continental Breakfast	ESB 1001
8:00-8:05AM	Overview of Activities for the Day	
8:05-9:00AM	Reports from the Break-out Groups on Basic Science Challenges	
9:00-11:00AM	Metals Basic Science Infrastructure	
9:00-9:45AM	Panel 2: Instrumentation	*Marc DeGraef, Kevin Fahey, Emmanuelle Marquis, Shef Baker
9:45-10:15AM	Coffee Break	ESB 1001
10:15-11:00AM	Panel 3: Materials Information and the Cyberinfrastructure	*Richard LeSar, Alessandro Mottura, Zi-Kui Liu, Vidvuds Ozolins
11:00-12:00PM	Education and Curriculum	
11:00-11:30AM	Panel 4: The Curriculum: What is the core of Materials Science and Engineering?	*John Lewandowski, Chris Schuh, David Bahr, Peter Voorhees, Eric Chason
11:30-12:00PM	Panel 5: The Future Undergraduate and Graduate Materials Engineers: What do they look like?	*Katherine Li, Jeff Evans, Bill Reynolds, Michael Sangid, Tobias Schaedler
12:00-1:00PM	Lunch	ESB 1001
1:00-3:30PM	Future of the Profession	
1:00-1:30PM	Panel 6: Workforce Needs: Present Status and Future Projections	*Wayne Jones, Eric Taleff, Don Shih, Harry Kington
1:30-2:00PM	Panel 7: Diversity and Broadening Participation in MMN	*Carol Handwerker, Wayne Jones, Liz Holm, Sung Kang
2:00-2:30PM	Panel 8: Supporting Early Career Professionals in MMN	*Michelle Manuel, Ellen Cerreta, Kip Findley, Dan Lewis
2:30-3:00PM	Coffee Break	ESB 1001
3:00-3:30PM	Panel 9: Research Modalities: Individual Investigators, Small Collaborative Groups and Large Programs	*Carlos Levi, Shef Baker, Tony Rollett, Diana Lados
3:30-3:45PM	Summary and Assembly of Break-out Sessions	
3:45-4:30PM	Break-out Sessions	
4:30-5:00PM	Break-out Reports and Wrap-up	

\* *Panel Chair and Coordinator*

## 2. Introduction: Grand Challenges and National Priorities

Fundamental research in metals and metallic nanostructures has led to some of the most profound science underlying the structure, processing and properties of materials. Linking atomic level interactions to interface motion, defect formation, and phase transformations has allowed us to transform metals and metal alloys into nano-, micro- and mesostructures, with exceptional control, performance, and stability. This research has transformed not only metal and metallic nanostructure research: it has provided the basis for understanding structure-dependent properties and processing of ceramics, semiconductors, composites, and complex, heterogeneous material structures at increasing length and time scales. NSF has played a major role in creating this knowledge and educating the field's leaders by "supporting fundamental research on the relationship between the structure and properties of metals and alloys"... "encompassing length scales from the atomic to the macroscopic, including the nano, micro and mesoscales."

In the next decade, fundamental research in metals and metallic nanostructures has the potential to continue to transform science into innovative materials, devices, and systems. Metals are everywhere, from steel, aluminum, and titanium for transportation and infrastructure to shape memory alloys for biomedical implants and metal nanoparticles as carriers for cancer detection and treatment. Though it is common to think of these only at the macroscale in terms of their application, all of these applications require control at the nanoscale to create and improve the properties for which they are known. Metals and metallic nanostructure research (MMN) reveals the physical and chemical laws governing phase transformations, the structures they create, and their resulting properties and integrates this knowledge into theory, computation and simulation, and materials design. While each application targets specific properties and performance, whether functional, structural, or biological, fundamental metals science creates a path for their design, manufacture, and use.

The societal and economic impacts of MMN research will continue to be significant: metals and metallic nanostructures are the basis for systems and technologies critical to solving national and global grand challenges. Innovative metals, metal alloys, and metallic nanostructures are needed to advance systems for

- energy generation, harvesting and storage - thermoelectrics, batteries, fuel cells, advanced turbines, magnetic induction, motors, hydrogen production and storage, nuclear reactor materials, separation membranes
- propulsion and transportation – high strength, high performance lightweight structures, materials designed for improved creep, impact, fatigue or corrosion resistance, high temperature metals, alloys and coatings for extreme environments, non-destructive evaluation
- electronics, telecommunication, and information technology – electronic packaging, process modeling, device nanostructures to overcome the end to

- Moore's law, thin film and nanostructured electrical interconnects, magnetic devices and motors, and sensors
- sustainability – nanostructured catalysts for catalytic convertors, polymer catalysis hydrogen and ammonia production, low pollution smelting and refining processes
  - health care – imaging systems, integrated in-vivo sensors, electronics, and communication systems for health monitoring and drug delivery, prosthetics and implant materials and systems, cancer treatment technologies
  - manufacturing - additive and nano-manufacturing technologies, non-equilibrium processing approaches, recycling and reuse, rapid deployment of alternatives to “critical” materials.

Fundamental and applied research in metals and metallic nanostructures is continuing to play a leading role in creating the informatics and simulation-based materials-innovation infrastructure embodied in the US Federal R&D Materials Genome Initiative (MGI) and the National Nanotechnology Initiative (NNI). The MGI was established in 2012 to leverage synergies between experimental and computational materials science and engineering research across multiple federal agencies supporting R&D in order to accelerate the pace of materials development. The central premise of MGI is that the period between materials discovery and their integration into new technologies and applications will be shortened by creating greater synergy between experimental and computational research and developing the infrastructure to support this translation. Likewise, the NNI is developing the scientific knowledge base for nanotechnology across materials systems, applications, and STEM disciplines and is translating this research into nano-enabled products, a scientific workforce trained in nanotechnology, and societal benefits as diverse as improved health care and national security.

The Workshop on Emerging Science and National Priorities in Metals and Metallic Nanostructures was held in June 2012 to identify significant research trends, fundamental science directions, and recent breakthroughs in MMN that will strengthen our ability to respond to these scientific challenges and national priorities. A central theme of the Workshop was the view that research in metals and metallic nanostructures has provided and will continue to provide benefit to the nation through the coupling of experiment, theory, and simulation to link atomistic, nanoscale, microscale, and mesoscale phenomena at time scales for an ever widening range of applications. Design of new metals and metallic nanostructures requires an understanding of the processes used to create them, their evolution over time, and in three dimensions with complex, realistic geometries. As identified in the Workshop, emerging theory, simulation, and experimental research approaches in metals and metallic nanostructures rely on advanced synthesis techniques, computational and characterization tools with unparalleled spatial and temporal resolution, and their integration for bridging length and time scales. Supporting this research and its promulgation into materials and systems is STEM education that reinforces a materials science and engineering view, creation of a community that nurtures early career scientists, particularly academics, and development of a materials science and engineering workforce able to support, advance, and apply MMN research approaches to ever broadening applications.

In this report we outline specific scientific opportunities enabled by emerging research in metals and metallic nanostructures, categorized in terms of

- 3-D and 4-D Materials Science
- Structure Evolution and the Challenge of Heterogeneous and Multicomponent Systems
- The Science Base for Property Prediction
- Nanoscale Phenomena at Surfaces – Experiment, Theory, Simulation
- Prediction and Control of the Morphology, Microstructure, and Properties of “Bulk” Nanostructured Metals
- Functionality and Control of Materials Far from Equilibrium
- Hybrid and Multifunctional Materials Assemblies
- Materials Discovery and Design - Enhancing the Theory – Simulation - Experiment Loop

These emerging opportunities are not meant to be all-inclusive, but illustrate the intellectual promise of metals and metallic nanostructure research, as well as its widening impact.

Finally, the workshop addressed critical issues limiting the U.S. Materials Research Infrastructure as well as Global Competitiveness, Education and Workforce Development.

### **3. Emerging Science and National Priorities in Metals and Metallic Nanostructures**

#### **3.1 3-D and 4-D Materials Science**

Control of structure across *all* length scales and over time is at the core of the design and discovery process for new metallic systems with unique functionality. In the context of materials science, the term “structure” at its most basic level encompasses not only the atomistic details of single phase materials, but also multiple phases, with their compositions, crystal structures, morphologies, crystallographic orientations, states of stress, and defects. The next level of “structure” encompasses the spatial relationship of these multiple phases and their interfaces and their evolution in time and space to create real materials with properties dependent on wide range of material lengthscales. The embodiment of structure and structure evolution into models of material function and properties is an urgent need for meeting US national research priorities, such as MGI and NNI. Predicting and characterizing structure in 3-D from the nanoscale to the mesoscale and its evolution over timescales ranging from picoseconds to multiple years (known as “4-D”) will require major scientific advances along all fronts - from new modeling and experimental approaches to new instrumentation with the requisite spatial and temporal resolution. Since modeling and measurement of structure and structure evolution require multi-dimensional representation, usually across multiple researchers, these advances

must be accompanied by an increasing ability to effectively and efficiently collect, integrate, analyze and share terabyte-scale datasets to capture materials structure in 3D and 4D. Through this approach the coupling between theory, experiments and modeling should be strengthened and the feedback loop shortened. Innovative modes for collaboration and use of unique (and usually expensive) instrumentation (with their complex datasets) will also need to be created and tested and the education process for materials students to learn to use these approaches and tools will need to be expanded and enhanced.

Newly emerging tomography techniques offer unprecedented levels of resolution and insight into material structure across the length scales [1]. At the high resolution end of the structural spectrum there have been remarkable developments in instrumentation for 3-D and 4-D materials science, including LEAP atom probe tomography and TEM-based electron tomography (including STEM with angular dark field imaging, vector field electron tomography as well as with conventional bright field and dark field imaging modes), hybrid ESEM-STEM tomography and dynamic transmission electron microscopy (DTEM) [2 – 6]. At higher length scales, synchrotron and lab-scale X-ray tomography using X-ray absorption, diffraction and phase contrast mechanisms now permit acquisition of structural, crystallographic and stress state information [7 – 9]. For structural, chemical and crystallographic information over larger material volumes, new capabilities in the areas of focused ion beam (FIB) tomography, automated mechanical serial sectioning and femtosecond laser-assisted tomography have also evolved dramatically [10 – 16]. These techniques, taken individually and in combination, are transforming the scientific linkages between processing, structure and property, permitting radical improvements in our ability to explain the processing and structural origins of a wide range of material properties. Examples of selected 3D datasets shown at the workshop are given in Fig. 1 [17 - 20]. These datasets illustrate the rich diversity of science challenges for metals structure research: void formation during processing of metal matrix composites, composition and phase zirconium alloys for nuclear fuel rod cladding, the character of grain boundary networks that result in crack initiation, and dislocation distributions in a Mo nanopillar.

Emerging 3-D and 4-D characterization techniques also bring a range of challenges with regard to the large size of the datasets, the fundamental issues regarding image reconstruction, and the ability to integrate data from multiple instrument sources into a complex representation of structure evolution [21]. Synchrotron experiments can easily generate terabyte-size datasets and, other than high capacity magnetic recording devices, there is no straightforward manner to transfer or share this volume of raw data. While it is often recognized that sample fabrication and data acquisition require substantial effort, the segmentation and reconstruction processes often require even more. Large datasets in X-ray, electron or optical approaches are collected with instrument operating parameters that are often selected without consideration of the challenges of segmentation and reconstruction. For any instrument the images gathered are a convolution of the true image, noise in the instrumentation system, the signal measured by the detector, and the algorithms used to extract the data from the signal. Reconstruction approaches that explicitly consider the physics-based instrument point

spread functions simultaneously with data collection could radically improve the speed of

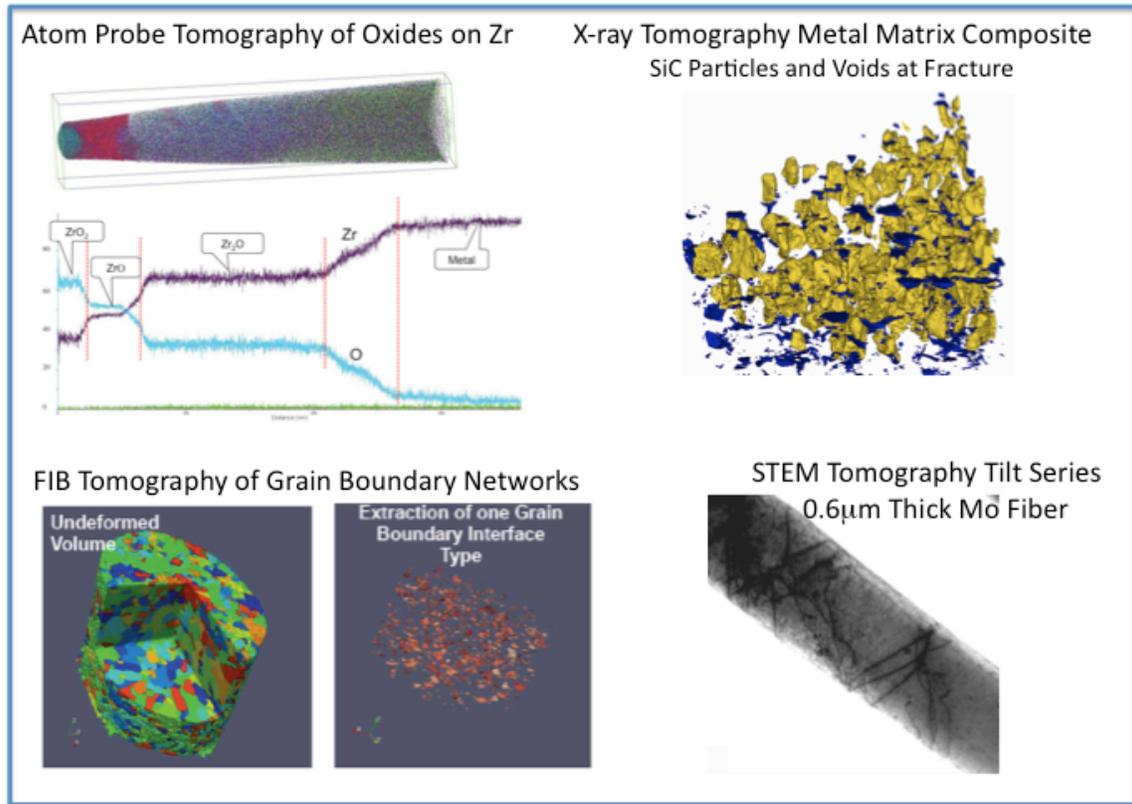


Fig. 1 Void formation during processing of metal matrix composites [17], composition and phase zirconium alloys for nuclear fuel rod cladding [18], the character of grain boundary networks that result in crack initiation [19], and dislocation distributions in a Mo nanopillar [20].

reconstruction and the quality of information gathered. Reconstruction approaches are also needed for integrating disparate datasets to recreate a microstructure, for example, by fusion of volumetric strain and crystallographic information from x-ray diffraction with 2-D multi-slice information on crystallographic orientation, microstructure, and composition datasets from SEM-based EBSD and EDS. Fundamental challenges still exist on the statistics of structure and the determination of the physical size of the representative volume element (RVE) that must be probed for prediction of a given property. While the RVE is typically considered as the smallest volume element of a material that can reproduce a macroscopic constitutive response, for properties that derive from a highly local response within a materials structure, the RVE is not yet well-defined. For example, it may be possible to define an RVE for assessment of the elastic properties of a heterogeneous material but not the fatigue strength or fracture toughness of the same material. Furthermore, mathematically rigorous, automated algorithms and workflows for meshing and analyzing complex microstructural and nanoscale features are needed in order to make the linkage to structure and evolving properties.

The volume of data that will be acquired by emerging, and as yet to be developed 3-D and 4-D techniques is enormous. All the relevant data for any materials system will be heterogeneous and, in many cases, distributed internationally across a range of institutions with specialized instrumentation. In this sense, “Big Data” challenges exist on all fronts, including capture, representation, analysis and storage of the 3-D and 4-D data. Resolving these challenges will require the combined expertise, collaboration, and support of multidisciplinary teams. The hub model for collaborating and sharing of information, notably demonstrated by the NSF-supported nanoHub [22], is an early demonstration of how some of the challenges in sharing simulation software, data, methods, and educational tools can be addressed to support the research community.

### **3.2. Structure Evolution and the Challenge of Heterogeneous and Multicomponent Systems**

The fundamental tenet that properties are determined by composition and structure demands that their evolution be predictable from materials design through the earliest stages of material processing and manufacturing and into service environments. The vastly varying timescales of structural evolution processes – nucleation from the solid, liquid, vapor and plasma states, growth of distinct domains, phases (stable and metastable) and grains and longer-timescale processes such as coarsening and evolution of structure due to externally imposed mechanical, chemical or electrical fields pose major challenges for full experimental characterization. Models for structure formation and evolution are thus essential, but are strongly challenged by the multicomponent character of the majority of metallic systems in use.

At the core of the structural evolution problem is the ability to predict behavior at the atomistic scale and make connections to the continuum scale descriptions. This requires fundamental knowledge of the thermodynamics and kinetics of transformations, which, in turn demands accurate thermodynamic models of multicomponent systems that are captured in validated databases. This has long been recognized by the Calphad community [22 - 25], though thermodynamic databases, while now commercially available, are incomplete due to the slow processes of generating and assessing experimental data and developing and validating models for the Gibbs free energy of multicomponent compounds that often depart from stoichiometry and contain defects. The process of experimentally mapping out these databases can itself lead to new materials discoveries. For example, a rigorous thermodynamic evaluation of the Co-Al-W ternary diagram in 2006 [26] resulted in the discovery of a new ternary  $L1_2$  phase,  $Co_3(Al,W)$ , which shows promise as a major constituent of metallic single crystals for high temperature applications [27]. Other multicomponent metallic systems suffer from incomplete knowledge of ternary and quaternary phase equilibria and of the many intermetallic compounds that could provide pathways for improving the functionality and structural performance of metal systems. Of particular note in this regard are alloys based on magnesium, the structural metal with not only the lowest density, but also excellent biocompatibility and resorbability for bio metal implants [28].

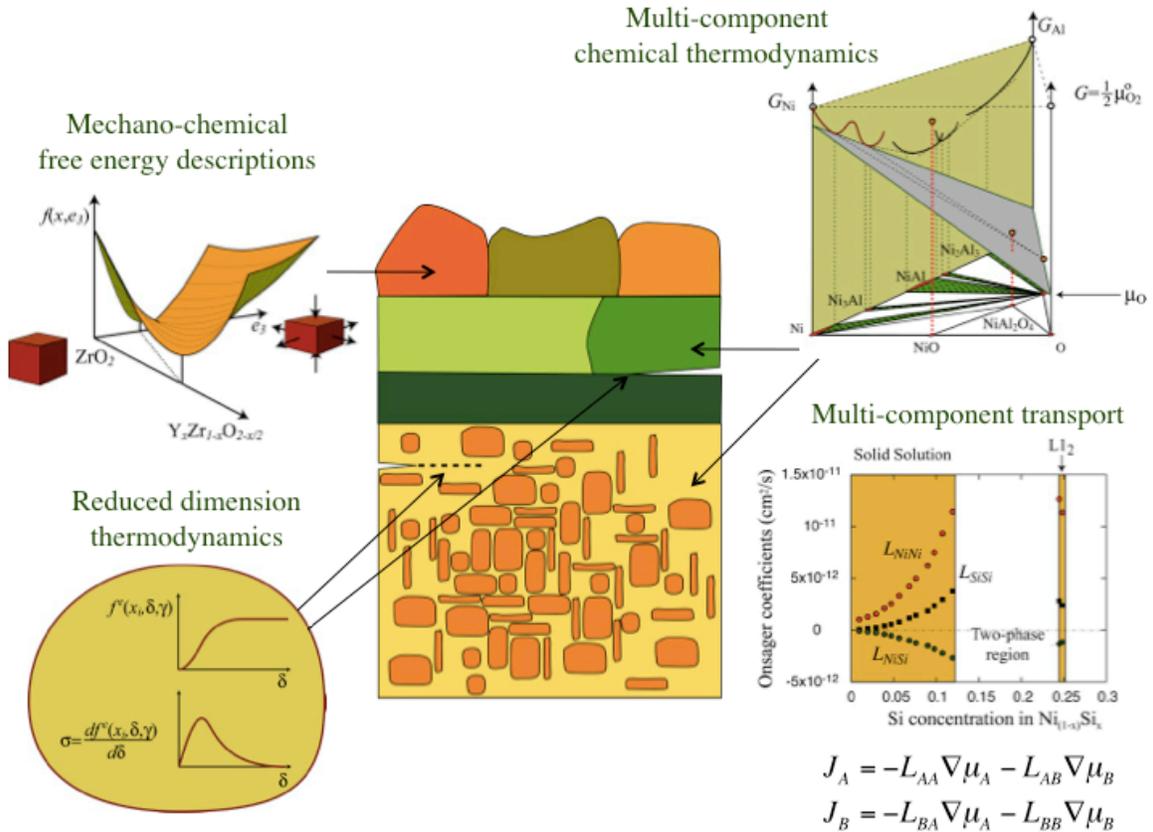


Figure 2 – A computational framework for integration of atomistics, thermodynamics (including stresses), interfaces and kinetics [33].

Beyond the thermodynamics of multicomponent systems is a realization that models and data for atomic and interface/grain boundary mobility and transformation kinetics are also needed to predict diffusion and structure evolution [24]. A combination of first principles analyses combined with experimental information is likely the most efficient path forward for thermodynamic and kinetic analyses of bulk materials [29, 30]. Materials dominated by the presence of high densities of interfaces, discussed in more detail later, present even greater challenges.

Ultimately the challenge, summarized in Fig. 2 [33], is to develop a computational framework that integrates atomistics, thermodynamics (including thermodynamic quantities beyond composition) and kinetics for bulk materials as well as their interfaces and that captures not only the features that determine important average properties but also those at the tails of the structural and compositional distributions that determine performance. Therefore, many aspects of structure evolution must also be addressed at the mesoscale. This includes, for example, the size, shape, spatial and orientation distributions of precipitates, the size and morphology of grains, or the size, shape, and spatial distribution of pores in porous materials. These structures are exquisitely dependent on the processing paths used to produce them and these paths frequently

involve time scales far in excess of those accessible in atomistic scale simulations. Given the importance of structure and composition in determining the properties of metallic materials, including nanostructured materials, and the inability of atomistic scale calculations in predicting the evolution of the structure of alloys, it is clear that additional methods are needed for the higher length scales.

The atomistics of diffusion are at the core of many structural evolution phenomena. In multicomponent systems a full description of diffusion phenomena requires information on system thermodynamics as well as on the local barriers to atomic transport, both for a single solute and in the presence of multiple solutes in concentrated quantities. Great strides have been made in first principles approaches for calculating hopping barriers in various metallic and intermetallic systems. Connections to continuum properties can be made via the use of cluster expansions combined with kinetic Monte Carlo approaches for the prediction of diffusion at finite temperatures [29, 31, 32]. Challenges remain for applying techniques to non-dilute multicomponent systems; new algorithms along with increased computer power should permit progress on this necessarily large computational problem. Large-scale calculations could ultimately identify appropriate “averaging” approaches as well as uncover new mechanisms in the presence of high gradients or high concentrations of point or line defects.

One approach that addresses the higher length scale is the phase field method, where the interface between domains is taken to be diffuse rather than sharp as in the classical approach. The phase field method employs coarse-grained free energies and the diffusive dynamics by which microstructure evolves in reality, and thus it can predict the evolution of the structure of a metal on the mesoscale. Since the method is based upon free energy functionals, it is possible to add other fields, such as elastic stress, magnetic or electric fields and include the effects of the many alloying elements that are typical in technical alloys. Thus the method provides a bridge between the atomistic and the continuum.

Much work remains to realize the full potential of the approach. The effects of the diffuse interface, usually taken much thicker than in reality for computational convenience, remain to be fully understood in many cases. Numerical methods employed to solve these nonlinear diffusion equations need to be developed, with particular attention to those methods that scale well on peta- and exa-scale computers. Although there has been significant progress at developing an open-access phase field code, FiPy from NIST, at this point there is no widely employed standard phase field code as there is for density functional theory or molecular dynamics. An important extension of the phase field method, known as the *phase field crystal* method, which captures atomic scale structure through use of an order parameter that represents local density, with the free energy functional minimized by a periodic order parameter configuration. This formulation allows consideration of grain orientation, interface structure, stresses, and compositional inhomogeneities but at the longer time scales required for diffusion, permitting semi-quantitative scaling of the properties of multocrystalline solidification, dislocation dynamics, fracture, grain boundary energetics (premelting), elastic phonon interactions, grain coarsening, linear and non-linear elasticity and plasticity [34 - 37].

While implemented in many different contexts, from a first-principles statistical mechanical point of view, phase field models can only be considered rigorous when applied to phase transformations and microstructure evolution involving phases that have a group-subgroup relationship, and then only if the coexisting phases are coherent. This includes phase separation between identical crystal structures, differing only in their concentration, as well as order-disorder transformations on a parent crystal structure (e.g.  $L1_2$  ordering within an fcc matrix). Since the coexisting phases are linked by a symmetry group/subgroup relationship, they can transition into each other through a continuous variation of suitably defined order parameters (e.g. composition or order-disorder order parameter). The continuity between the phases allows for the formation of diffuse interfaces separating the coexisting phases. The existence of a symmetry group/subgroup relationship also means that the various phases competing for stability correspond to local minima of a common free energy surface, with interfacial free energies arising from contributions of the homogenous free energy supplemented with a gradient energy correction introduced in the original Cahn-Hilliard-Allen theories. A large number of phase transformations do not involve symmetry group/subgroup relationships, but instead involve phases that are crystallographically very different, necessitating sharp or incoherent interfaces. Due to incompatibilities in symmetry, the various phases cannot be described by a single free energy surface from which interfacial free energies can be extracted. Instead the various phases have their own free energy descriptions and the sharp interfaces separating them will have a corresponding excess free energy. Phase evolution then generally involves diffusion within the individual phases coupled with interface migration driven by chemical potential and stress differences across the interface. The description of these phase transformations with phase field models can be viewed only as phenomenological as there is no clear coarse graining procedure available to link the actual crystallographic and atomic scale processes to the parameters of the phase field model. More appropriate approaches, though numerically substantially more challenging, are based on sharp interface models, which can be treated, for example, with level set methods.

Rigorous models for structure evolution will ultimately permit tailoring of multicomponent materials, from the mesoscale down to the nanoscale, for optimal properties. For instance, in magnetic alloy systems, nanostructured soft magnetic alloys and nanocomposite permanent magnets rely on the magnetic exchange correlation length as a fundamental length scale. When microstructures consist of nanoscale grains, the resulting coincidence of correlation lengths results in remarkable properties in soft ferromagnetic materials [38]. However, the preparation of multi-phase, multi-component nanostructured materials for use in bulk form (at higher scale structures) is extremely difficult due to the coarsening driving forces, presenting significant challenges for control of structure and structure evolution. Alloy and process design, assisted by a modeling infrastructure could identify multicomponent, multiphase systems that enable revolutionary improvements in materials performance, especially in power dense conversion and conditioning technologies with greater energy efficiency. Anticipated trends in the performance of magnetic materials, as tracked by the coercivity, that are possible with multicomponent, nanostructured materials are shown in Fig. 3 [39]. Similar discoveries would be anticipated within a vast array of multicomponent materials, including thermoelectric systems based on intermetallics, battery cathode materials, fuel

cell membranes and catalysts, piezoelectrics, multiferroics, hydrogen storage systems, shape memory alloys and lightweight, high temperature structural materials.

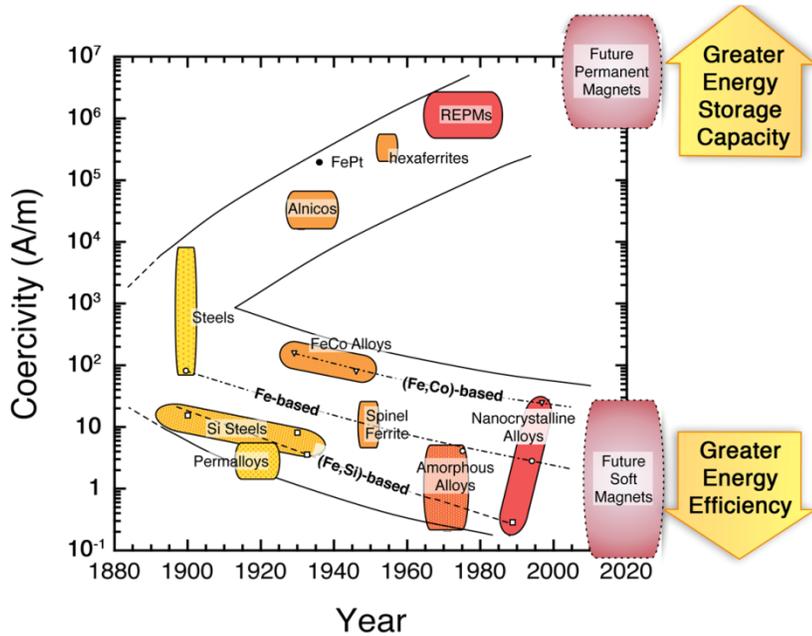


Figure 3: Timeline of progress in the improved performance for soft and hard magnets as measured by the coercivity of different magnetic materials [adapted from [39]].

### 3.3 The Science Base for Property Prediction across Length Scales

The convergence of new structural characterization capabilities, new theory and vastly improved computational capabilities promises a new era for material property prediction. A wide combination of properties are needed simultaneously for most materials to be employed in any engineering system, ranging from properties such as the melting temperature to properties such as fatigue, where the extremes of microstructure dominate the response, Fig. 4. Although a wide range of properties have traditionally been classified as “structure insensitive” this paradigm fails at specific size scales for specific properties. One well-known example is the decrease in melting temperature with decreasing particle size, i.e. the Gibbs-Thompson effect. In addition to the scale and structure dependence of properties, many properties are more sensitive to rare features of material structure rather than the “average” structure that would be captured in a random 2-D section. It is, therefore, important to predict not only “average” properties, but also the “minimum” properties and the associated rare, but critical features that limit design and material performance.

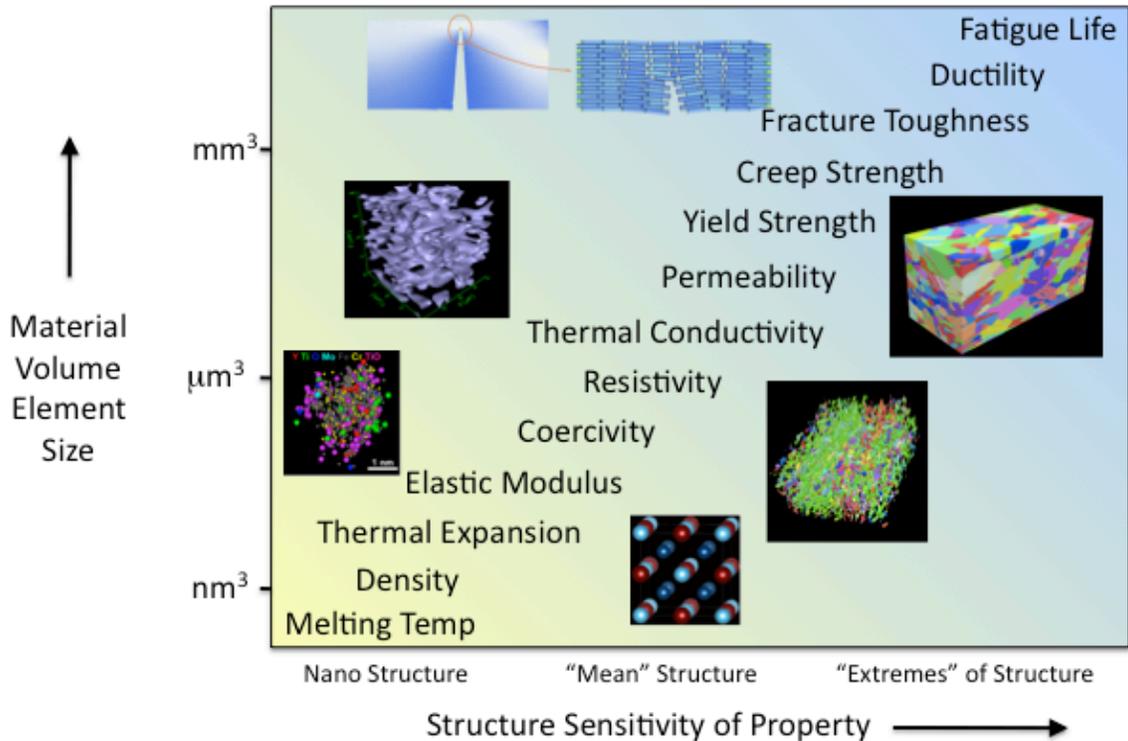


Figure 4 - The volume element of material relevant to the prediction of a spectrum of material properties [40].

The new 3-D imaging modalities discussed above promise the capability of sampling statistically significant volumes of material, capturing features on the extremes of the distribution of structural features, thereby acquiring structural information for the “average” as well as the “minimum” property. New statistical approaches to sampling large datasets, including the statistics of extremes, are needed with careful consideration of the representative volume element required for any given property – perhaps best referred to as the “property volume element” [41, 42]. Such considerations will undoubtedly drive the development of new instruments and expand the functionality of existing 3-D characterization approaches and motivate advances in modeling of composition and structure evolution, as noted in the previous section. A related issue is the level of information that should be retained about 3-D structure for any given material, since in principle a new design scenario could always change the RVE. Compressive sensing approaches, yet to be applied in any level of detail to materials problems, represent one potentially useful area for further investigation [43].

Prediction of a significant set of properties for a material requires material information across a wide range of length scales. Connecting information across scales is most often done with “information passing” in which information at a smaller scale is represented so as to reduce the amount and complexity of the information. That reduced representation, which generally is a reduced-order model, is then passed to the next scale [44]. The use of reduced-order models creates errors in the information passed from lower to higher

scales. Since there are few inverse models that go down in scales, the information flows in only one direction, which inhibits our ability to use the current state at the higher scale to help define the information needed from the lower scale. There are many challenges and uncertainties in the “information passing” paradigm. It implicitly assumes that there exist natural coarse-graining lengths at each scale and ignores overlaps of scales, which may not be appropriate in many situations. The reduced-order models add uncertainty when used to describe phenomena at larger scales [44]. Coarse graining ignores rare and extreme events and structures, limiting their ability to describe such important phenomena as failure. The challenge is that we have no *a priori* knowledge of which variables at a small scale are of critical value at a larger scale. Indeed, the vast majority of variables may have no information value at a larger scale and it is inefficient to measure or calculate all them. Research is needed to develop new experimental and modeling approaches to identify that critical information.

Metallic materials are pervasive in engineering systems in part due to their ability to under plastic deformation without catastrophic failure. The monotonic and cyclic plastic properties of materials (yield strength, hardening rate, creep, fatigue) are all sensitive to dislocation motion as well as the interaction of dislocations with structural features of the material. Predicting the collective behavior of dislocations and their resultant effect on mechanical properties and failure processes remains a major challenge for metallic materials [45]. Dislocation phenomena occur over a range of timescales, with fast glide processes that can result in stochastic bursts of dislocation activity [46] along with slower relaxation phenomena such as dislocation climb. Under cyclic deformation conditions, a fractional portion of the gliding dislocations exhibit irreversible behavior upon reversed loading, resulting in their storage in slip bands that eventually lead to failure. Many aspects of the dynamic behavior of dislocations and the resultant storage and annihilation processes remain to be understood. For example, the role of dislocations sources in the heterogeneity of small-strain plasticity, the dynamics of plasticity in small volumes and the generation and interaction of dislocations with interfaces are all areas that require more detailed investigation. Given the typical lengths and timescales relevant to dislocation processes, the method of choice for simulations has been one in which the entities of the simulations are not atoms, but rather the dislocations themselves, i.e. Discrete Dislocation Dynamics (DDD). The computational framework for DDD has reached a level of maturity for some problems, primarily where the plastically deforming volumes are highly constrained, such as in micropillars [47 - 56] and thin films [57 - 64], Fig 5.

Major challenges remain for DDD simulations of bulk plastic deformation processes. Dislocation dynamics simulations include all atomistic – dislocation core-level events in terms of models, including dislocation reactions, such as annihilation and junction formation, as well as all activated processes, such as processes that have an energy barrier and are thus thermally activated. In the latter category are the well-known processes of cross slip and climb. The classical models implemented to date, for example the Escaig model of cross slip [65 - 67], do not capture the complexity of dislocation substructure evolution, suggesting that further investigations of these fundamental aspects of plastic deformation are needed. Recent atomistic simulations have provided new insights,

providing new directions for development of this modeling approach [68, 69]. It is anticipated that DDD simulations will provide insights to small strain and high rate deformation, ultimately guiding the development of macroscale constitutive models (for

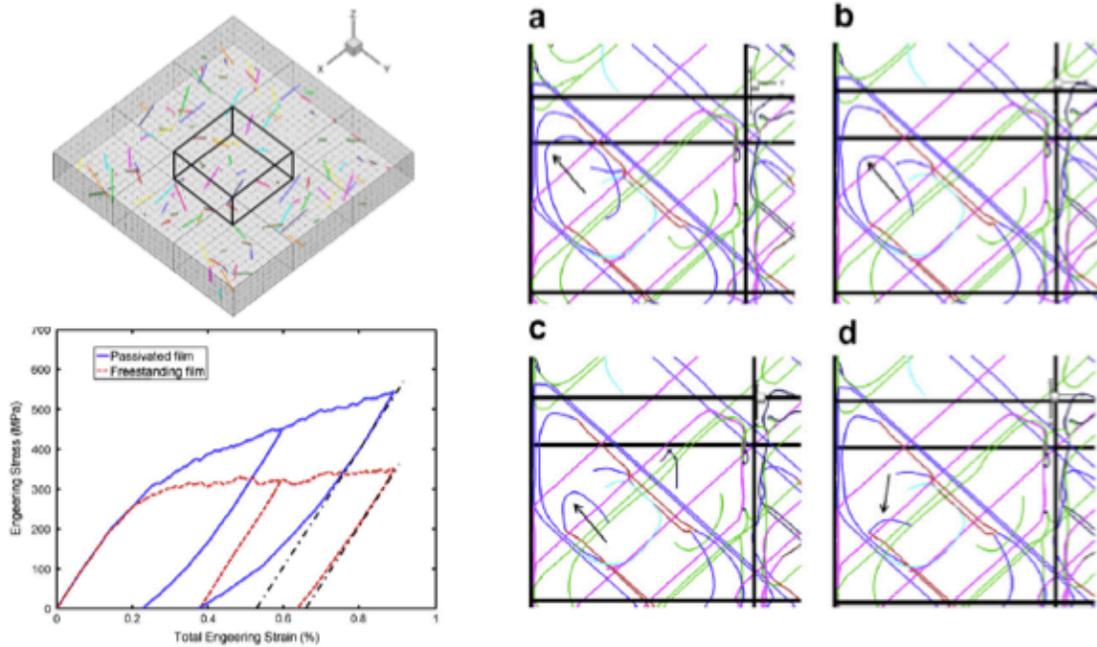


Figure 5 - Computational framework for DDD has reached a level of maturity for some problems, primarily where the plastically deforming volumes are highly constrained, such as in micropillars [47 - 56] and thin films [57 - 64],

example, crystal plasticity models) for monotonic and cyclic deformation. Beyond this, theory that can guide the prediction of other statistical aspects of deformation, such as the tendency toward avalanche behavior [46] remain to be incorporated into property prediction frameworks. At the mesoscale, plasticity is still challenged by an incomplete understanding of slip transmission across interfaces and boundaries. One promising approach in quantifying slip transmission and the role of interfaces and grain boundaries in localizing strain is in combining molecular dynamics simulations and measurements of a large set of grain boundaries, with a range of incident slip types and orientations, as shown in Figure 6 [70]. The simulated energy barriers for transmission have direct implications to modeling crystal plasticity, fatigue, fracture and creep at the mesoscale for specific metal structures. Crystal plasticity approaches are effective for predicting the evolution of texture at large strains in fcc metals [71], but less effective at predicting small-strain behavior on a grain-by-grain basis [72]. The degree to which factors such as elastic anisotropy, the distribution of dislocation sources and three dimensional microstructural “neighborhoods” (that in the limit could be characterized via n-point statistics) influence low strain behavior remains to be investigated in more detail with close linkage of experiment and theory.

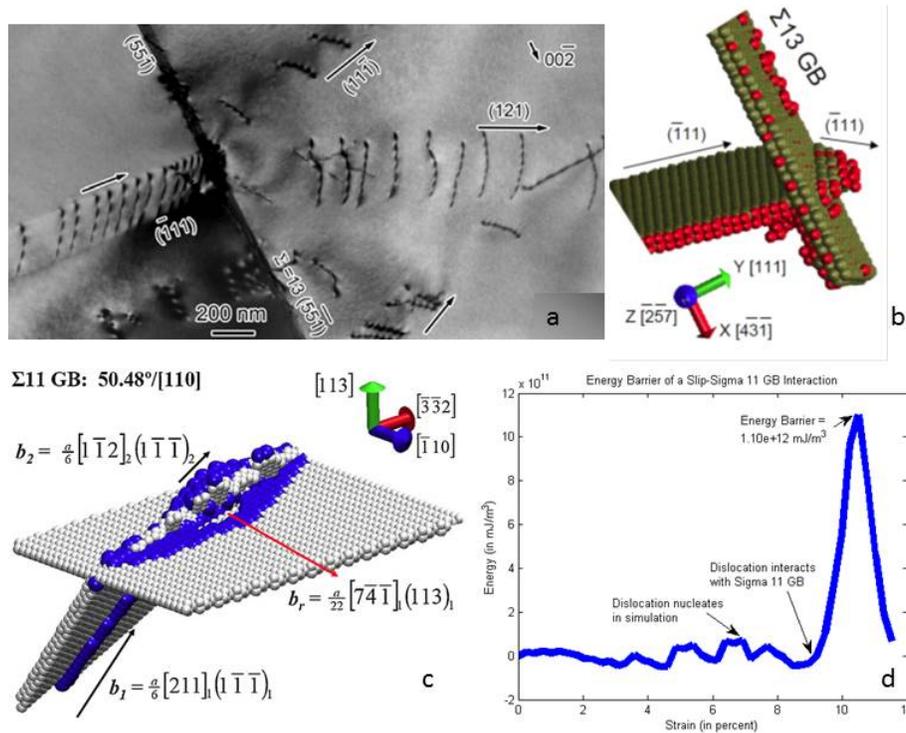


Figure 6 - (a) In situ TEM micrograph of slip transmission in a low stacking fault energy material for a  $\Sigma 13$  GB. (Micrograph is a composite figure formed from images in which the diffraction condition was specific to each grain as described in (b) MD simulations of slip transmission through a  $\Sigma 13$  GB compare well with the experimental results. Interactions of dislocations with  $\Sigma 11$  GB with the resulting dislocation reactions and the corresponding energy barrier calculations for slip to penetrate the  $\Sigma 11$  GB. [70]

Functional materials including thermoelectrics, magnetic materials, shape memory alloys, catalysts and electrodes for fuel cells and batteries could greatly benefit from research aimed at fundamental properties underlying their function. As computational power continues to improve, the ability to calculate the properties of more complex, multicomponent materials within the framework of density functional theory improves. However, the temperature dependence of properties and the kinetic phenomena that intervene in these systems are areas that remain in need of fundamental research. Also, as discussed in more detail below, the ability to model interfaces and their effect on properties remains a major fundamental barrier, particularly for functional materials, where applications often demand submicrometer-scale layering or percolated structures with specific geometries for optimal properties.

With respect to the translation of new materials into engineering applications, success in property modeling and prediction translates to dramatically reduced amounts of testing, eliminating the need for expensive and time-consuming “design of experiments” approaches that are currently widely practiced in industry [73]. Testing will instead be driven by the needs for model development and for verification and validation of these

models, for bulk materials as well as for nano-scale structures. This, in turn, is likely to motivate new site specific, *in-situ* and/or rapid testing techniques for the spectrum of metallic materials and properties of interest.

### **3.4. Local Phenomena at Interfaces – Experiment, Theory, Simulation**

Recent research on the structure and stability of metal surfaces, interfaces and defects, and their motion and interaction with the environment has implications for our understanding and control of atomic-scale and molecular-scale reactions and for creating new materials with dramatically improved functionalities and properties. Metals are used in contact with aqueous solutions and other liquids - in biological environments, in many electrochemical energy technologies, and in structural applications. In some cases, electrochemical potentials are applied or generated across these interfaces, but these simply add to the generally complex chemistries ubiquitously in play. In structural applications, these potentials manifest themselves as corrosion, especially in lightweight structural alloys containing high percentages of reactive metals. For energy conversion in batteries, fuel cells, and capacitors, they enable the charging and discharging chemistries and processes, which often involve dissolution and re-deposition of a metal. A variety of distinct phenomena, they are connected generally by a common structure of a metal/electrolyte interface whose local properties control the aggregate response of the material. Throughout the workshop, the science that underlies these developments was discussed.

Understanding the interaction of metal surfaces and interfaces with fluid environments is clearly a challenge in many research areas and for many fundamental processes. For example, the coupling of chemistry, electrochemistry, crystallography, and mechanical properties in determination of the performance of metal surfaces used as electrodes for batteries or fuel cells, and even catalysts, is complex. While the essential interface processes are the same at surfaces and interfaces at all size scales, from bulk materials to nanoparticles and nanoporous films, the atomic scale features and configurations that exist on highly curved or chemically heterogeneous surfaces have been found to profoundly influence their activity with the environment. Charge transfer, the growth of passivating or poisoning layers, and surface reconstruction also have significant impact on the performance, stability, and reliability of materials. As a result of the growing ability to track atomic and electron transport at and along surfaces, as well as their local surface structures and strains, it is becoming possible to design surfaces at the nanoscale with specific features, such as kinks and steps, and to stabilize such structures through controlled segregation and composition control.

One example illustrating the potential of this holistic approach at the nanoscale is in the atomic origins of the high catalytic activity of nanoporous gold [74-76]. Their measurements of the 3D surface structure, composition, and strain of nanoporous gold revealed (1) the likely mechanisms for the unexpectedly high catalytic activity of nanoparticle Au and nanoporous Au in CO oxidation reactions and (2) a fabrication pathway for compositionally tunable nanostructures that are stable to coarsening during

catalysis. Nanoporous gold catalysts are self-supporting films formed by dealloying Au-Ag films. The resulting bicontinuous 3D nanostructures have surfaces with positive and negative curvatures, with large curvature gradients between them. Nanoparticle gold has been observed to lose its catalytic activity at a much smaller characteristic feature length than nanoporous gold, which suggested the importance of local interface structure. For nanoporous gold, its high catalytic activity was found to be associated with the density of geometrically necessary kinks and steps required to transition from positive to negative curvatures, their stabilization and suppression of (111) faceting by residual segregated Ag, and 5-10% out-of-plane positive strains near the surface. Going beyond the traditionally planar view of interfaces into a structurally and compositionally rich 3D view at the nanoscale will provide not only a more accurate picture of the underlying thermodynamics and kinetic processes, but also greater prediction and control of interfaces for future applications.

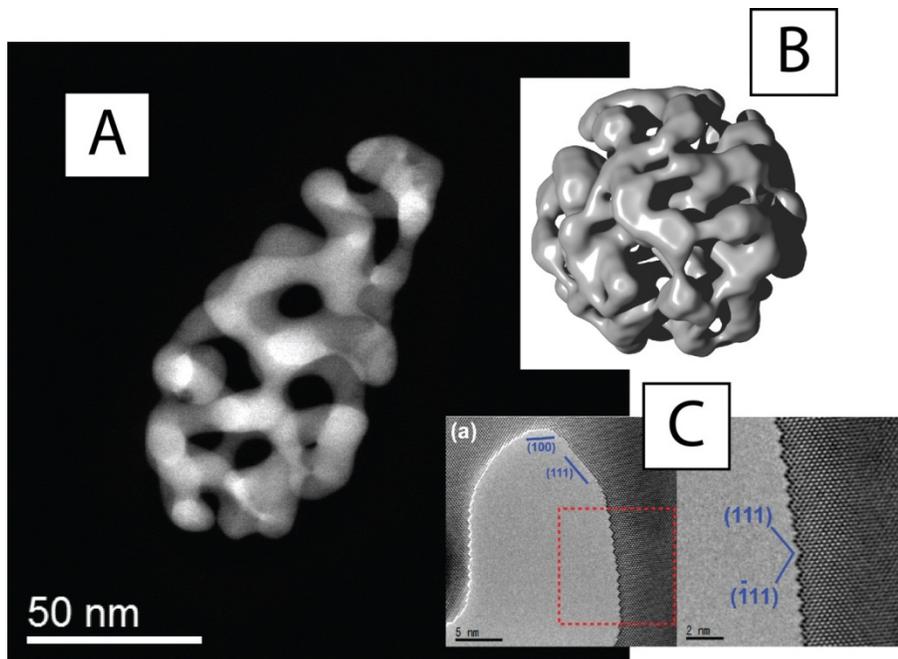


Figure 7 - Different synthetic, computational, and characterization tools applied to the study of “nanoporous gold,” made by electrochemical dealloying. (A) Transmission electron microscopy (TEM) showing dissolution of silver from silver/gold nanoparticles yielding nanoporous nanoparticles that exhibit unusual nanoscale-related kinetics and morphological evolution. (B) Large-scale atomistic kinetic Monte Carlo simulations combined with novel image processing methods leading to a theoretical understanding of these materials. (c) Atomic resolution environmental TEM of nanoporous gold revealing origin of its catalytic activity: here, the presence of a CO background pressure is shown to induce a faceting reconstruction in high-gold content materials, suppressing CO oxidation. [74-76].

Some important aspects of the fundamental science of metal/electrolyte interfaces, for example, include (a) surface mobility of metal atoms along the interface [77-78], (b)

dissolution of the surface [79], (c) deposition on the surface [80-82], and (d) reaction chemistry [83-84]. Such fundamental physical phenomena inform slightly higher-level phenomena such as nucleation and growth of nanoparticles [85-87], morphological stability [88-89], and corrosion [90]. Modeling methods, such as first principles models of the metal/electrolyte interface [91] and characterization tools, such as in situ TEM [92], are in their infancy.

A challenge not limited to nanoscale processes at metal surfaces is to design experiments and models that can be coupled along time and length scales. Development of the theory-simulation-experimental linkages that can reveal the mechanisms of metal interface reactivity, stability, performance, and reliability is a scientific grand challenge in this area. Such advances are needed for application to the broad range of metals and environments noted above. For example, while many examples exist of the extension of a model to attempt to account for bulk electrical performance of a battery, the use of general metal-electrode interface parameters suggests rightly so that the actual processes are still unknown in many cases.

Similarly the need for high speed characterization methods, to match time scales for diffusion calls for the further advances in ultra-fast microscopy, as well as the development of more “bulk” techniques. Matching the size scale of interface reaction experiments, such as through scanning probe techniques and environmental TEM, and the time scale with molecular dynamics, phase field, and phase field crystal simulations of the metal and its surrounding environment will be critical to determining the mechanisms that lead to the performance and long term stability of these systems.

Another related, but distinct, area of importance is in matching the characterization environment with the relevant experimental and application environments. With the increasing use of atom probe tomography, atomic resolution TEM, and environmental TEM, it is becoming clear that the structures so often captured in UHV or “dry” environments may not be the actual structures present during interactions with “dirty” real environments in other laboratory experiments or in use. Surface re-organization and reconstruction, adsorption and dissolution, and metastable phase formation are all processes that change interfaces. The continuing development of new techniques that can deal with increasingly complex environments will enrich both the underlying scientific base as well as the ability to create and field new metals, metal nanostructures, and even new technologies. One such innovative, even futuristic, technology described at the Workshop was electrochemically self-propelled multi-segmented nanowire motors and swarming nanoparticles envisioned for biomedical applications.

### **3.5. Prediction and Control of the Morphology, Microstructure, and Mechanical Properties of “Bulk” Nanostructured Metals**

“Bulk” nanostructured metals, that is, metals that can be used for structural applications but possess a structure that is controlled at or near the nanoscale, will be central in a variety of applications related to the subject areas of energy, environment, and sustainability. Nanostructure research is, therefore, not just limited to the creation and

behavior of individual nanoparticles or nanostructures, but must include the formation and resulting properties of nanoscale to mesoscale assemblies of nanostructured materials. Examples of this length scale linkage include:

- the yield criteria for nanostructured metals and thin films, their damage evolution, multi-axial stress state effects, strain rate dependence, and their stability and behavior as a function of temperature,
- the role of environment in plastic response of nanostructured metals;
- the failure and fatigue of nanostructured metals and thin films, and their durability in extreme environments, and
- the ability to fabricate precise “bulk” nanostructured materials in 3D, especially with multiple components, phases and classes of materials.

While there are many applications of such research, two are highlighted here. One possible application is in radiation tolerant metals needed for next-generation nuclear power generation, and ultimately for fusion reactors. Strategies for success in this area include fabrication of metals with both adequate strength and a continuing ability over time to absorb point defects formed by radiation, both properties potentially aided by nanoscale precipitates, grains and/or nanolaminate configurations [93-94]. A second application is in new magnetic nanoscale materials that can serve as rare-earth magnet substitutes [95].

Developing and maintaining nanostructure features in bulk materials is a very rich area of fundamental metals research, including

- laboratory synthesis of bulk nanostructured metals,
- stability under different driving forces,
- characterization of bulk nanostructured materials at the needed spatial and temporal resolution without relaxing the physical constraints needed to preserve their “bulk” character, and
- theory and computational methods that can help inform and even drive the experimental work.

Fundamental knowledge regarding the structure dependence of surface and interfacial energies, phase diagrams, and interface mobilities are lacking, as is diffusion in the bulk, on surfaces, and along grain boundaries. These factors ultimately determine the microstructures that can be obtained starting from nanoscale features. For example, a model for the stability of binary nanocrystalline alloys with respect to grain growth and phase separation was recently developed and used to construct “nanostructure stability maps” with several new types of stable nanostructures identified [96, 97]. Likewise, molecular dynamics simulations of nanocrystalline, multicomponent alloys using angular-dependent interatomic potentials, such as in the Cu-Ta system, are revealing segregation and nano clustering effects that pin grain boundaries, prevent grain growth, and thereby stabilize nanostructures and create stronger materials than if the alloying agents were uniformly distributed [98, 99]. Experimental examination of these models’ predictions will likely reveal here-to-fore unidentified effects of composition and structure on the stability of nanocrystalline materials. With research targets such as those

noted here, research on “bulk” nanostructured materials fits well within the MGI and NNI goals. Ultimately for translation into applications, the linkage between structure and engineering properties (e.g., constitutive relations) is also needed, in addition to the more fundamental chemical and physical linkages between synthesis and structure.

Three central research directions have been identified for “bulk” nanostructured materials. First, new techniques are being developed to characterize materials at unprecedented levels of detail, such as X-ray and TEM tomography, the many variations of serial sectioning, and high-speed in situ microscopy. Such characterization is yielding new information about grain orientation, stress states, strength hardening precipitate locations, and dislocation distributions, all with the necessary spatial and temporal resolution. For progress to continue, particularly for materials mechanics research, the data and modeling challenges described above in *3D and 4D Materials Science* must be resolved. Second, measurements of the properties of nanostructured materials necessitate new *fabrication* approaches, as exemplified by techniques such as focused ion beam milling (FIB) of micropillars that are subsequently compression tested and imaged *in-situ* within the scanning electron microscope, Fig. 8 [100]. Third, useful scientific knowledge will be found only if the interpretation of such experiments rests on a firm foundation of mechanics theory, much of which is lacking for nanostructured materials.

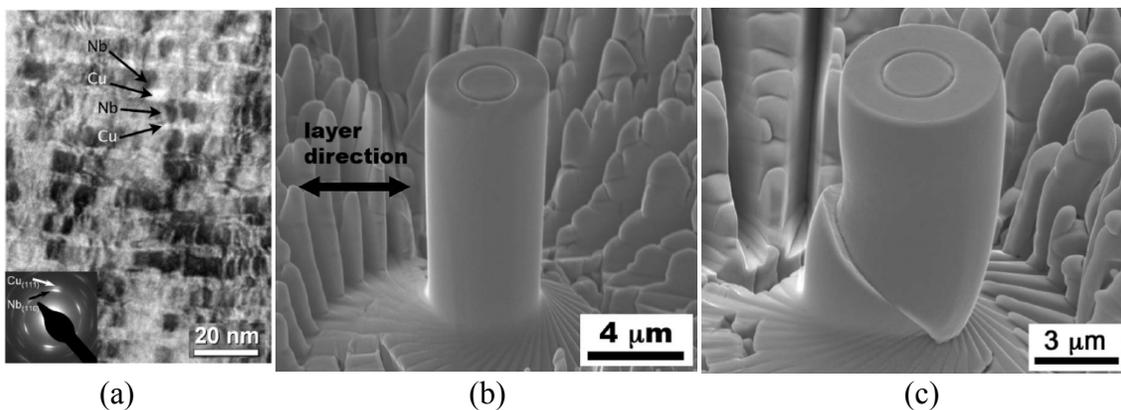


Fig 8. TEM bright-field micrograph of as-deposited 40nmCu/40nmNb nanolaminate material. Selected area diffraction pattern showing  $\{111\}\text{Cu} \parallel 110\{\text{Nb}\}$  interface texture (a), an as-fabricated micropillar (b) and a micropillar that underwent 25% compression before failing by catastrophic shear [100].

### 3.6. Functionality and Control of Materials Far from Equilibrium

The ability to predict and control local driving forces for diffusion and interface motion in systems far from equilibrium permits design and creation of structures at the atomic, nanometer, and micrometer scales. By applying such control, new fabrication pathways are providing access to novel glassy structures, nanoparticles, nanowires, and thin films with equally novel properties, functionalities, and applications. For example, the understanding of atomic configurations in the glassy state and crystallization kinetics as a function of cooling rate have advanced the discovery of large sets of rare-earth containing

and Fe-rich bulk metallic glasses with unique mechanical, magnetic and corrosion properties. In another example, nanoscale core-shell precipitates formed by a two-step heat treatment, whereby the core formed at high temperature provides a template for growth of the shell at lower temperature, Fig. 9a, represents the promise of non-equilibrium paths for improving material properties. For the example of AlLiSc core-shell precipitates, this structure leads to an improved resistance in irradiation environments [101]. Exploiting the full potential of materials far from equilibrium will require an improved understanding of phase and structure stability, nucleation, and the thermodynamics and kinetics of diffusion and interface motion at surfaces, highly curved interfaces and complex grain boundaries. Additional examples are presented here that illustrate the possible impact of research in this area on both scientific understanding and applications of the resulting nanostructures and thin films.

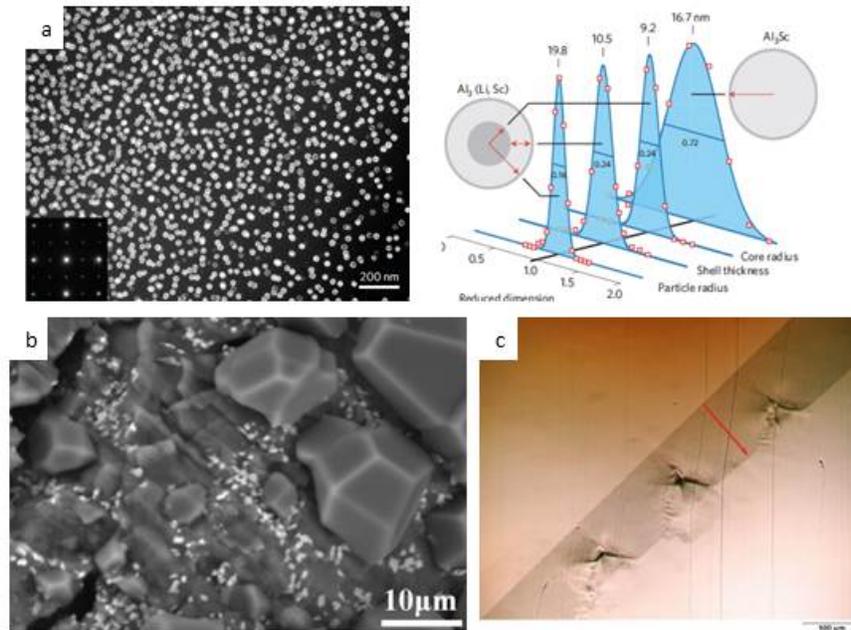


Fig. 9 – (a) TEM dark field micrograph (left) showing a highly uniform distribution of core-shell AlLiSc precipitates with  $L12$  structure. The selected area diffraction pattern inset shows strong fcc reflections and weaker  $L12$  superlattice reflections in a square pattern typical of an  $h001i$  crystal orientation. Particle size distributions (right) narrower in core, shell and core-shell sizes in the present alloy much narrower than in typical AlSc binary alloy particples.[101] (b) SEM images of large crystal formation after the first hydrogenation cycle of a highly deformed Mg-Ni alloy [102] (c) Optical micrograph of an Al bicrystal showing the coupling between shear and grain boundary migration and the generation and growth of new grains during migration of  $76.3^\circ \langle 100 \rangle$  tilt grain boundary after annealing at  $370^\circ\text{C}$  for 60 min under a tensile stress of 0.84 MPa. [103]

Nearly defect-free, high aspect ratio metal nanowires have been fabricated through low supersaturation growth (MBE) on oxidized and unoxidized silicon single crystals partially coated with carbon [104]. The faceted nanowires were observed to grow predominantly from the metal/substrate interface (from the base of the nanowire), with nanowire nucleation occurring where the substrate was not covered by carbon. This technique does not require patterning of the substrate, construction of channels for

deposition that must subsequently be removed to leave free-standing nanowires, or the presence of catalyst particles such as in vapor-liquid-solid (VLS) or vapor-solid-solid (VSS growth). Furthermore, the structural evolution during the nanowire formation process must be related in an inverse way, to grain growth and dewetting of polycrystalline thin films on substrates [105,106].

Complex pattern formation during dewetting of epitaxial single crystal metal films on substrates (Ni on MgO [107, 108] and Au/Fe on sapphire [109]) is beginning to reveal both the competitive processes involved in dewetting, grain growth, and thermal stress relaxation and the control in pattern formation achievable from the nanoscale through the mesoscale. Crystallographic effects, as well as hole nucleation from surface defects, are key in destabilizing thin film systems. The formation of large faceted crystals during grain growth and dewetting of thin films during hydrogenation of Mg also suggests the importance of stress-induced coarsening to thin film stability in the presence of a phase change [102].

Research on modeling and measuring stress generation and relaxation in thin films by competing processes during thin film formation [110], thermal cycling [111], applied stresses [103] or isothermal stress generation processes, such as intermetallic formation during room temperature annealing of Sn films on Cu [113-116], is revealing the role of microstructural heterogeneity and crystalline anisotropy on the response of different thin films to stress. Further progress will require more detailed understanding of how grain boundaries and interfaces migrate and respond to applied stresses, the mechanisms and conditions for coupling stress and grain boundary motion, and the ability of grain boundaries and surfaces to act as vacancy sources and sinks for diffusional creep [112, 113]. In the future this research will be important to producing stable, high performance alloy film applications as diverse as solar cells and microelectronics to catalysts to corrosion-protection and thermal barrier layers.

### **3.7. Hybrid and Multifunctional Materials Assemblies**

Hybrid combinations of metals with other materials classes assembled into designed structural elements such as Kagome lattices, truss or honeycomb structures, sandwich panels, foams or zero or negative thermal expansion structures have the potential to expand property space, filling voids that are naturally present with monolithic materials. An example of the expansion of potentially accessible properties in strength – density space is given by Ashby [117]. Using hybrid structures to expand the design space for other combinations of properties could result in vast array of new systems with integrated electrical, thermal, optical and/or mechanical functionalities. An example of a nickel truss structure with a density of approximately  $10 \text{ mg/cm}^3$  is shown in Fig. 10 [118]. This structure, fabricated by a self-propagating photopolymer waveguide technique followed by nickel electrodeposition, can recover from >50% compression and demonstrates large energy absorption under cyclic loading conditions. Folding and morphing structures constructed from metallic systems potentially offer for additional dimensions of control and functionality in sensors, microsystems as well as in larger structures [119].

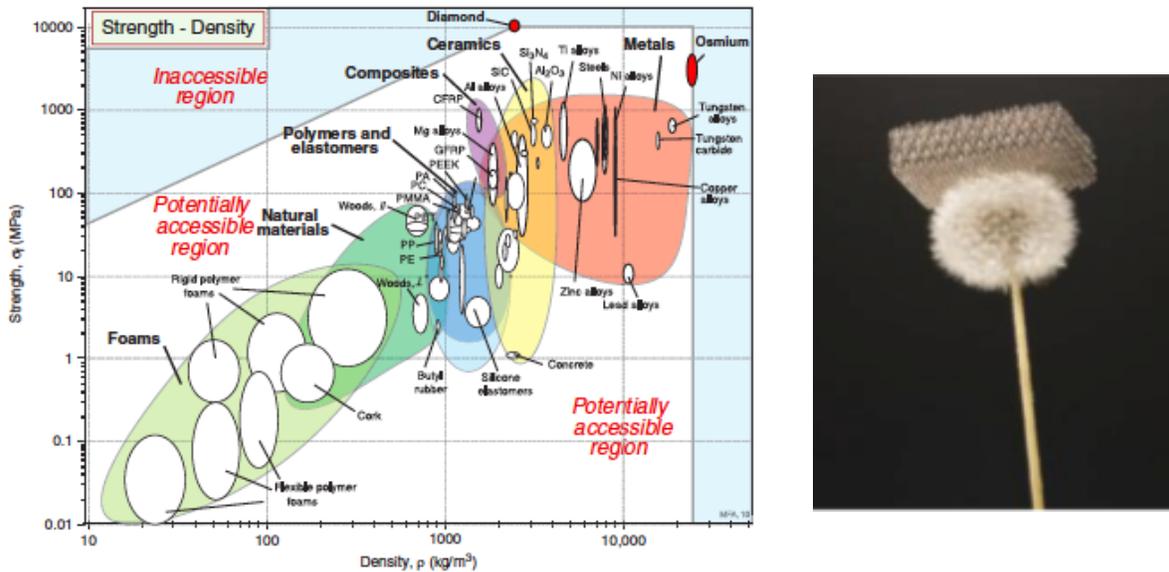


Figure 10. Potentially accessible property space that can be accessed by hybrid structures (a), adapted from [117] and ultralight weight metallic truss structure [118].

While the promise of hybrid multifunctional systems is immense, there are wide-ranging technical challenges yet to be addressed. Among these is first the problem of structural and topological optimization that jointly considers the constraints of synthesis processes. For example, a complex distribution of two sets of materials may optimize a property, but the resolution of a 3-D printing process may not be sufficient. There are many gaps in the basic understanding of the additive, digital and 3-D manufacturing processes that will ultimately enable this class of materials. The physical processes that permit layer-by-layer deposition in general are still not well enough understood to select processing parameters or predict final properties. Basic understanding of the energy deposition processes and material response to electron and laser beams is needed for progress in processing across a wide range of materials systems. Beyond this, selective fusion of powder particles, sintering, photopolymerization, local melting within packed powder arrays and the flow of viscous binder-powder mixtures all require further study. Given that melting and sintering are often embodied in the processing, residual stresses also become a major consideration; improved process models must address these issues, as the experimental parameter space is very large.

### 3.8. Materials Discovery and Design: Enhancing the Theory – Simulation - Experiment Loop

The computational resources that have recently become widely available to researchers are changing the landscape for materials discovery and design. Atomistic calculations with density functional theory can now efficiently guide the search for multicomponent materials with desirable electronic, thermal, elastic or thermodynamic properties. An example of this highlighted at the workshop centered on thermoelectrics, where materials based on PbTe currently exhibit some of the highest levels of the figure of merit, ZT. While it is known that higher order additions of solute can further improve the properties,

the potential experimental search space is large and it is difficult to experimentally isolate the effects of solute on thermal conductivity (due to anharmonic phonon scattering, which is correlated with a high Grueneisen parameter or alternatively due to the formation of nano-scale precipitates) compared to electrical conductivity (due to favorable band structures). Starting with PbTe, band structures and the Grueneisen parameters were quickly calculated for 72 ABX<sub>2</sub> compounds, permitting systematic selection of compositions for experimental synthesis and thermal conductivity measurements, Fig. 11. Fabrication of high quality experimental materials for screening purposes is extraordinarily time consuming and computational tools enable a feedback loop that greatly reduces the timescale required for searching for promising new materials [73].

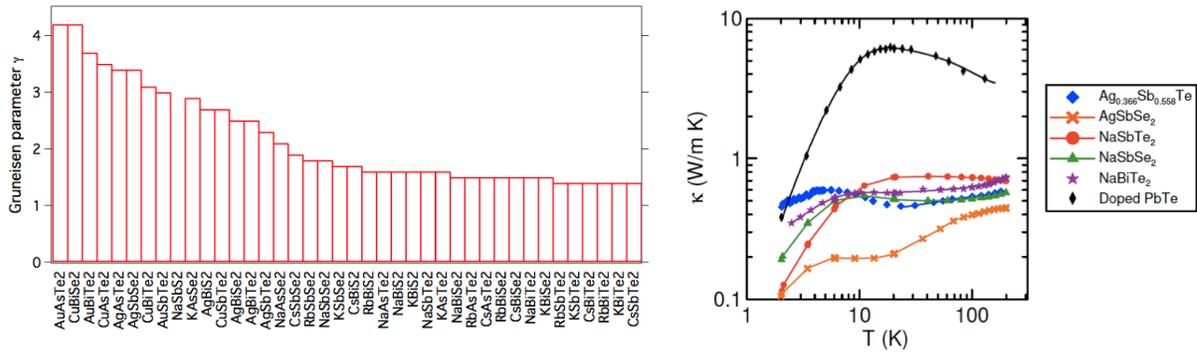


Figure 11 – Systematic ab-initio calculations for screening of systems for new thermoelectrics and the results of experiments on most promising candidates [adapted from 120].

Since materials must typically exhibit a suite of favorable properties, rather than a single property, rigorous models are needed for properties sensitive to material structure across the lengthscales, Fig. 4. As discussed earlier, the availability of 3-D and 4-D structural data will be an essential element of progress on this front. Protocols for passing only essential structural information from one length scale to the next and one property model to the next are needed. Where models for material behavior are not yet predictive, a close coupling between experiment, theory and modeling can greatly accelerate their development and validation. Additionally, where physical models are lacking, informatics tools that extract information from the vast array of materials literature and develop correlations between processing, structures and response, at and across scales need development. Accelerating materials discovery and development will not only require computational tools, but also experimental tools for property measurement that can efficiently and rapidly measure properties at the appropriate lengthscale. For example, as nanostructured materials emerge, some properties will need to be measured at this scale. An example from the workshop of a MEMS-scale device developed for testing nanowhiskers is shown in Fig. 12. New, high throughput rapid characterization techniques for a variety of transport properties have also recently emerged [121, 122]. Expanded, rapid approaches for site-specific measurement of a broader array of properties could also dramatically expand the search space for new metallic and

nanostructured materials. Finally, it is recognized that an efficient theory – computation - experiment feedback loop will typically require a pairwise research interaction of researchers, at a minimum. Resources for groups of two or three investigators would strongly enhance this approach.

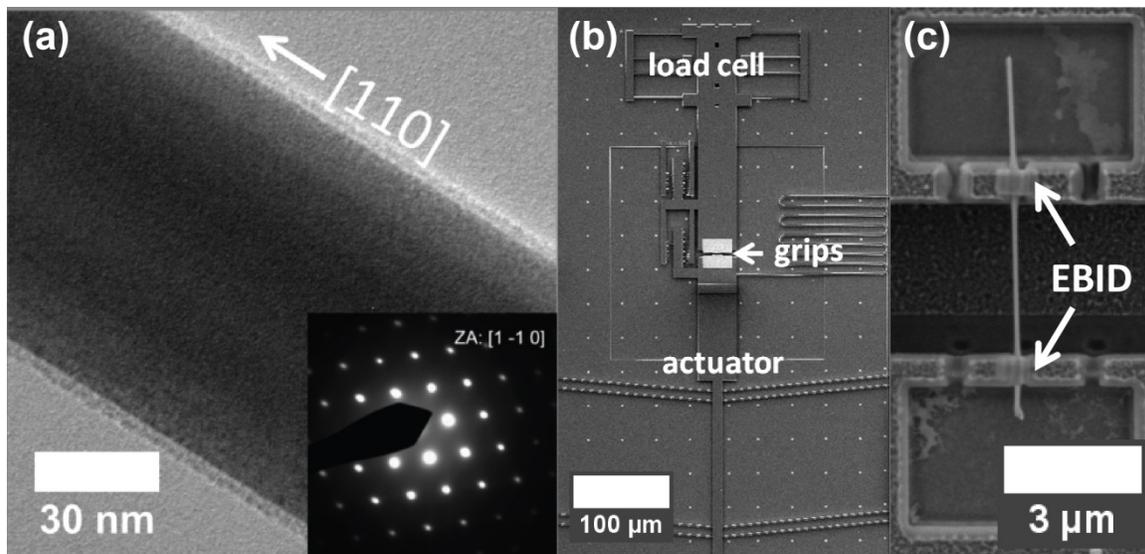


Figure 12 – Small scale testing of Pd nanowhiskers [123].

#### 4. Materials Research Infrastructure

Critical to continued advances in materials research is the availability of a wide spectrum of advanced instrumentation. As the complexity and the spatial, temporal and chemical sensitivity of materials research instruments continues to increase, the cost of acquiring and maintaining these instruments also increases. The state-of-the-art transmission electron microscope is an example of an instrument that has traditionally existed within the individual infrastructures of nearly all materials research institutions. However, the most recent generation of aberration corrected transmission electron microscopes are priced well beyond the resources of most individual institutions. Often, not a single instrument, but suites of new instruments are required to tackle emerging materials research problems. For example, 3-D atom probe tomography may require not only a new atom probe instrument, but also a focused ion beam microscope for sample preparation and TEM for characterization of the resulting sample. As NSF is *the* major source of resources for instrumentation, a thoughtful long-term materials instrumentation plan with substantial community input is essential for the US to maintain leadership in this critical area of science and engineering. The Major Research Instrumentation (MRI) Program plays an essential and critical role for materials instrumentation. However, programs that support smaller-scale instrumentation have been scaled back; an example of this is the now inactive Instrumentation for Material Research program. MRSEC programs commit significant resources to instrumentation, and this continues to be a major benefit to institutions with these programs. Unquestionably the availability of

more grant opportunities for small to intermediate scale instrumentation would have a strong, positive impact on the materials community, particularly for junior researchers who are in the process of building laboratories.

In recognition that some types of instrumentation are beyond the resources of individual institutions, NSF also supports National Facilities. These facilities are national assets, providing valuable access to state of the art techniques; among these are the Cornell High Energy Synchrotron Sources and the National High Field Magnetic Laboratory. An integrated network approach has been taken by NSF in its support of the National Nanofabrication Infrastructure Network (NNIN). Internationally, the emergence of multiple synchrotron facilities also highlights the trend toward centralization of instruments, requiring that investigators identify resources for travel in order to access these opportunities. Given these trends, it is important that NSF consider offering small-scale grants to graduate students, postdoctoral students and junior faculty to ensure access as well as to enhance the training of the future materials research workforce. In parallel, since specialized instruments are not limited to the US, such programs could enhance the international research experiences for these junior investigators.

Connected to the advanced materials instrumentation are the “Big Data” and Instrument “Forward Modeling” challenges mentioned in previous sections. As an example, one week of synchrotron experiments often produces so much data that as much as 6 months to a year is required for processing. The lack of an agreed upon materials taxonomy and metadata structure for a given instrument represents a barrier. “In-line” data analysis and reconstruction would also permit more efficient utilization of instruments. There are still basic research issues that limit the merging of data collected on a given material with different instruments in spite of the fact that parallel “data channels” would substantially enhance the understanding a wide spectrum of materials phenomena. Again, such complex problems may require multidisciplinary interactions, with the strong participation by NSF.

## **5. Global Competitiveness, Education and Workforce Development**

Research in the area of metals and metallic nanostructures will continue to have broad impact on a wide range of science and engineering challenges, but only if the future workforce is prepared to function in a rapidly changing environment. Foremost in the development of our future workforce is the training of students at the undergraduate and graduate levels. The Materials Science and Engineering curriculum has undergone a continuous and very substantial evolution over the past four decades, evolving early “materials specific” programs such as metallurgical engineering or ceramics engineering to curricula that cover the full spectrum of materials. Undergraduate curricula now contain the hallmarks of materials science and engineering: structure, properties, processing and performance. Required courses on the fundamentals in these areas tend to span the spectrum of materials classes without significant depth in specific systems, i.e. metals, ceramics, or soft materials.

For metals and metallic nanostructures, in particular, upper level undergraduate courses are needed that link length and time scales for processes. Capstone design courses focus on the engineering aspects of materials and often emphasize the importance of design teams in that context.

At the graduate level incoming students often have undergraduate degrees in other fields, i.e., physics, chemistry or electrical, mechanical, chemical or biomedical engineering, and thus have limited background in materials science and engineering. For this reason core courses at the graduate level have become increasingly important for sustaining and defining the important role of materials science and engineering as a distinct discipline. Externally, the Materials Genome Initiative and the need for integration of materials science with design of engineering systems motivate a stronger component of modeling and simulation at all length scales, uncertainty quantification and informatics at both the graduate and undergraduate level. Incorporating these topics into an already crowded and increasingly broad materials curriculum has proven to be challenging [124]. There are notable efforts to integrate computation into the curriculum in the context of design [125], but these are not yet pervasive. Considerable time and effort will be required to place Materials Science and Engineering computational expertise of undergraduate and graduate students on equal footing with other engineering disciplines. Alternative curriculum development mechanisms are needed and NSF can play a key role in this area via support of Summer Schools, Workshops and Curriculum Development activities. Rigorous evaluation of new programs and approaches should be integral to these new activities. Professional societies can play an increasingly important role in convening and supporting such community building activities for undergraduate and graduate students.

A strong future workforce should naturally be diverse in gender, ethnicity and geography. Historical trends in diversity in materials science from ASEE 2007-2011 data show essentially no change in the percentage of women and historically underrepresented groups in tenured and tenure-track faculty positions or receiving B.S. and Ph.D. degrees over that time period [126]. Diversity in the student body will remain a challenge without role models; achieving diversity at the faculty level is critical for future progress. This is a challenge given the long timeline of faculty careers. For this reason mentoring of junior faculty is critical. With the broadening of the materials science and engineering field, junior faculty (many of whom are recipients of CAREER Awards) report that it is increasingly unlikely that appropriate technical mentors exist within their own departments. NSF could have a major impact on mentoring and future diversity by developing programs that facilitate cross-institutional mentoring. Since professional societies provide venues where mentoring could naturally occur, they could also play a key role in meeting this need.

Future global competitiveness will require professionals strongly educated in the fundamentals with additional skills for operating in interdisciplinary and international environments. In this context, research internships can substantially enhance the educational experience of both undergraduate and graduate materials students. Many large industrial organizations support US-based internship programs as a future

investment in workforce. Unfortunately these programs rarely offer similar opportunities internationally. In smaller industrial organizations, the cost of intern support often inhibits student hiring. Innovative programs that provide incentives for hiring research interns could have a substantial positive effect on students as well as on the industry partners. At the graduate level, international research internships can provide access to unique instrumentation as well as foster other positive outcomes for graduate students, including long-term collaborations, patents, invitations for research lectures, and career opportunities, such as post-doctoral positions. While NSF has recognized the importance of international collaborations in programs such as the World Materials Network, the Partnership for International Research and Education (PIRE), and the International Materials Institutes; continued strong support will be needed to have a long-term impact on the development of the materials science workforce.

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