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Major Goals: The major goal of this project was to develop a set of guidelines for designing nanocrystalline alloys with structural stability that arises not due to a kinetic effect, which may be overcome with time, but due to a thermodynamic minimum in energy that is reliable. Specifically, the project sought to develop the alloy design principles for such thermodynamic stability for the entire periodic table of metals, including the alloy pairs that have negative heats of mixing and form compounds in equilibrium. These alloys are especially challenging to model in the nanostructured state, given that they can form more possible ground states that compete against a nanocrystalline state with grain boundary segregation. It was the specific goal of this project to expand our understanding of segregation-based stabilization of nanostructure to include such alloys.

The specific task lines of the project formed subgoals on a path towards such detailed understanding. One task line was focused on the development of a set of computational tools for alloy design in nanostructured systems. These tools increased in sophistication as the project progressed, and have been used to propose new alloys with predicted nanostructure stability. In parallel, experiments in the PI's laboratory and with collaborators explored the alloys predicted by the computational program. These explorations validated and informed the models, and also led to materials processing strategies that have scalability and commercialization potential.

Accomplishments: Theoretical Program

The first main outcome of the computational team on this project has been the development of a more rigorous and general criterion for nanocrystalline stability. By connecting the thermodynamics of grain boundary “complexions” (i.e., specific atomic structures that are energetically preferred) with those of bulk phase thermodynamics, we were able to develop the first nanostructure stability criterion against both grain growth and ordered compound formation, in accessible thermodynamic parameters. This major accomplishment was published in the final project year in Acta Materialia (v132 p128) and is a capstone to the years of theoretical work in this space. For binary alloys, this development presents a milestone as the first ‘complete’ model for nanostructure stability, a first-pass screening tool for any possible binary pair.

Beyond the first-pass stability criterion, there is a need for more detailed predictions before alloys are synthesized. For example, the criterion described above does not directly provide information on how the stability is affected by the composition and temperature of the alloy. To assess this, we have developed a Monte Carlo simulation capable of simultaneously exploring alloy configurations that are nanocrystalline, contain ordered compounds or solid solutions, or are single crystalline. The result is a tool that provides complete phase diagrams for systems with stable nanostructured phases, a result published in the final project year in an invited feature paper in JMR (v32 p1993).

In the future, nanostructured alloys will certainly involve ternary and multinary additions; these are nontrivial extensions to the existing theoretical state-of-the-art. We have recently started to expand our work to consider ternary alloys in the hope of submitting a future ARO proposal on this topic. In our final project year, we began to lay the first theoretical underpinnings for the ternary problem with a publication on the extension of our Monte Carlo method to multicomponent systems in Scripta Materialia (v127 p136), and a specific case study on a specific ternary alloy (Ni-W-Ti) described in more detail in the experimental section below.

Experimental Program

This project was built on an experimental philosophy of validation and verification of theoretically-driven expectations. In a number of cases, we worked with collaborators to leverage their processing expertise to test specific alloy design hypotheses.

1. Iron based alloys

The team has explored Fe-based alloys both internally in the PI's laboratory (by powder metallurgy) and in collaboration with a team at Sandia National Laboratory (SNL, by vapor deposition). Using our modeling tools, we predicted that with an alloying addition level of order 10%, Fe-Mg would be a system with a preference for nanostructure, and by comparison Fe-Cu would be a system expected to coarsen to macroscopic scales. As a first test of the model's ability to differentiate such systems in a side-by-side comparison, we collaborated with SNL to produce sputtered films of both alloys, and examine their thermal stability upon heating in situ in a transmission electron microscope. Whereas the Fe-Cu system indeed coarsened out of the nanostructured range rapidly at low temperatures, the Fe-Mg system was verified as having remarkable stability; in both cases the match between the experiments and the simulations was very strong. This work was published in 2016 in JOM (v68 p1625).

Having validated Fe-Mg as a potentially stable nanocrystalline alloy, Fe-Mg alloy powders with different compositions were created using high energy ball milling for 15 hours. X-ray diffraction (XRD), transmission electron microscopy (TEM), and atom probe tomography (APT) were used to determine the grain sizes and elemental distributions after milling and subsequent annealing. Characterizations clearly showed nanocrystalline Fe grains surrounded by Mg enriched grain boundaries. What is more, a stable grain size of around 45 nm was achieved due to the grain boundary segregation of Mg. This work was published in the final project year in Acta Mater. (v144 p447).

2. Hf-based alloys

We used our Monte Carlo algorithms to predict that the Hf-Ti system might be a stable nanostructure former, and collaborated with Prof. Andrea Hodge of USC to validate this using sputtered coatings. We were able to demonstrate that both by directly alloying with Ti, or by allowing interdiffusion to occur in multilayer stacks, nanostructured Hf could be produced with Ti decorating the grain boundaries and stabilizing the nanostructure. The Monte Carlo simulations matched very well with the experiments, and the demonstration of multiple processing pathways to a similar structure again suggests the importance of thermodynamics in determination of the preferred alloy structure in these alloys. This work was published in 2016 in Acta Mater (v108 p8).

3. Ti-based alloys

Based on the models, Ti-Mg alloy powders with different amounts of Mg were explored using high energy ball milling for 20 hours to produce nano-duplex structures. XRD and TEM measurements showed grains of Ti supersaturated with Mg and average sizes of 10-16 nm. Cold compressed samples were subsequently annealed for 8 hours at 500°C in high-purity argon gas in a thermomechanical analyzer to track the relative change of densification and thus the sintering behavior. TEM measurements of the resulting compacts demonstrated a well-developed nano-duplex structure of Ti grains and Mg rich particles with grain sizes of around 100 nm, evolved under conditions that also led to the consolidation of the powders to very high densities (over 90% relative).

4. Ni-Ti-W Alloys

In two prior ARO funded projects, the PI developed, in the first, electrodeposited alloys based on the Ni-W system, and in the second, powder metallurgy alloys based on W-Ti. As a first foray for our efforts in ternary alloys, it seemed reasonable to consider the combined effects of these two systems in the Ni-Ti-W system. This is because whereas W favors grain boundaries in Ni, and Ti favors grain boundaries in W, the Ni-Ti interaction is a negative heat of mixing, compound forming proposition. Indeed, the stoichiometric NiTi compound is the basis of the market-dominant Nitinol shape memory alloy. To study this ternary system we collaborated with Dr. Aslan Ahadi and his team at NIMS in Japan, for their expertise in sputtering NiTi-based shape memory films. With Dr. Ahadi, we were able to experimentally test our prediction of the formation of two different types of grain boundary complexions amongst NiTi ordered grains in this system. Upon heating in a TEM, Dr. Ahadi demonstrated the complexion transition that we had hoped to see, driven by entropy, in a ternary system with ordered compounds. This system thus tested every theoretical advance of the project (ternary system, ordered compounds, negative heats of mixing, and entropic effects). It presented a very nice capstone to the effort, and the side-by-side comparison of model and experiment was just published in Acta Mater (v142 p181).

In all of the above work, it is considered a major success of the program that the modeling guided the experiments, and in every case led to substantial validation. The application of our methods to deposition and powder processing shows the generality of the concept, and opens many pathways for scaling as well.

Training Opportunities: The project has trained a variety of students and postdocs.

The MIT Graduate Students on this project enjoyed training in thermodynamic theory, computational materials science, and collaboration with experimentalists, all of which contributed to their growth and maturation as scientific leaders.

Dr. Mansoo Park and Dr. Tongjai Chookajorn both began their Ph.D. careers under previous ARO grant support and finished their work on this program. They both returned to their home countries and became staff scientists at national laboratories there.

Dr. Zack Cordero and Dr. Michael Gibson enjoyed partial support under this program for the final years of their time at MIT. Prof. Cordero is now Assistant Professor at Rice University, and Dr. Gibson leads the materials team at Desktop Metal, an additive manufacturing company.

Arvind Kalidindi and Wenting Xing are current Ph.D. students both slated to graduate this coming year (2018). They enjoyed primary support from this program.

The program also engaged two visiting graduate students, Josef Hazi from Oxford and Peter Larsen from DTU Denmark. Both conducted research that contributed to their thesis at their home institutions.

The MIT Post Doctoral personnel on this project, Kathrin Graetz and Dor Amram, were supported to push the experimental program on Ti and Fe alloys, respectively. Dr. Graetz matriculated and became a staff scientist at a company in Austria, and Dr. Amram is still working at MIT on this program and transitioning to a new project.

Results Dissemination: Papers published in peer-reviewed journals:

1. A.R. Kalidindi, C.A. Schuh. “A compound unit method for incorporating ordered compounds into lattice models of alloys”, Computational Materials Science, 118, 172-179, 2016.
2. B.G. Clark, K. Hattar, M.T. Marshall, T. Chookajorn, B.L Boyce, C.A. Schuh. “Thermal stability comparison of nanocrystalline Fe-based binary alloy pairs”, JOM, 68, 1625-1633, 2016.
3. M.N. Polyakov, T. Chookajorn, M. Mecklenburg, C.A. Schuh, A.M. Hodge. “Sputtered Hf-Ti nanostructures: A segregation and temperature stability study”, Acta Materialia, 108, 8-16, 2016.
4. Y. Chen, C. A. Schuh. “Grain boundary networks in nanocrystalline alloys from atom probe tomography quantization and autocorrelation mapping”, physica status solidi (a), 212, 2302-2308, 2015.
5. M.A. Gibson, C.A. Schuh. “A survey of ab-initio calculations shows that segregation-induced grain boundary embrittlement is predicted by bond-breaking arguments”, Scripta Materialia, 113, 55-58, 2016.
6. Cordero, Z.C., B.E. Knight, and C.A. Schuh, “Six Decades of the Hall-Petch Effect – A Survey of Grain-Size Strengthening Studies on Pure Metals”, International Materials Reviews, 61, 495-512, 2016
7. Cordero, Z.C., R.R. Carpenter, C.A. Schuh and B.E. Schuster, “Sub-scale Ballistic Testing of an Ultrafine Grained Tungsten Alloy into Concrete Targets”, International Journal of Impact Engineering, 91, 1-5, 2016
8. Kalidindi, A.R., T. Chookajorn, and C.A. Schuh, “Nanocrystalline Materials at Equilibrium: A Thermodynamic Review”, JOM (Journal of the Minerals, Metals and Materials Society), 67, 2834-43, 2015
9. Xing, W., A.R. Kalidindi, and C.A. Schuh “Preferred Nanocrystalline Configurations in Ternary and Multicomponent Alloys”, Scripta Materialia, 127, 136-140, 2017
10. Kalidindi, A. and C.A. Schuh, “Stability Criteria for Nanocrystalline Alloys”, Acta Materialia, 132, 128-137, Acta Materialia, 2017
11. Kalidindi, A. and C.A. Schuh, “Phase Transitions in Stable Nanocrystalline Alloys”, Journal of Materials Research, Invited Feature Paper, 32, 1993-2002, 2017
12. Larsen, P.M., A.R. Kalidindi, S. Schmidt, and C.A. Schuh, “Alloy Design as an Inverse Problem of Cluster Expansion Models”, Acta Materialia, 139, 254-260, 2017
13. Amram, D. and C.A. Schuh, “Interplay Between Thermodynamic and Kinetic Stabilization Mechanisms in Nanocrystalline Fe-Mg Alloys”, Acta Materialia, 144, 447-458, 2018
14. Park, M., T. Chookajorn, and C.A. Schuh, “Nano-Phase Separation Sintering in Nanostructure-Stable vs. Bulk-Stable Alloys”, Acta Materialia, 145, 123-133 2018

Presentations at workshops, conferences, seminars:

1. Kalidindi, A.R., Schuh, C.A., 2015. “Stability of nanocrystalline alloys against grain growth and ordered compound formation,” MRS Fall Meeting, November 30-December 3, Boston, Massachusetts.
2. Kalidindi, A.R., Schuh, C.A., 2016 “Equilibrium grain boundary segregation in compound forming alloys” Gordon Research Conference: Structural Nanomaterials, July 10-15, Hong Kong, China.
3. Graetz, K., Schuh, C.A., 2016 “Processing and thermal stability of nano-duplex Titanium alloys” Gordon Research Conference: Structural Nanomaterials, July 10-15, Hong Kong, China.
4. Schuh, C.A. 2015 "Nanocrystalline Metals Stabilized for Commercial Use”, DuPont Central Research Facility, Wilmington DE, USA, June 2015
5. Schuh, C.A. 2015, “The Future of Nanocrystalline Metals in Theory and in Practice”, The 2015 Howard K. Birnbaum Memorial Lecture, University of Illinois, Urbana-Champaign
6. Schuh, C.A. 2015, “Entropic Stabilization of Duplex Nanostructured Alloys”, The 4th International Workshop on Interfaces at Bear Creek, Macungie PA
7. Schuh, C.A. 2016, “Processing Design Considerations for Nanocrystalline Alloys Prepared by Severe Plastic Straining”, Keynote Lecture, International Symposium on Plasticity, Kona HI
8. Schuh, C.A. 2016, “Grain Boundary Alloying in Nanocrystalline Metals in Theory and in Practice”, Mechanical Engineering Seminar, Brigham Young University, Provo UT
9. Schuh, C.A. 2016, “Nano-Duplex Alloys: A Family of Stable Nanocrystalline Materials Amenable to Rapid Sintering”, Symposium on Bulk Processing of Nanostructure Powders and Nanopowders by Consolidation, Opening Keynote Address, TMS Annual Meeting, Nashville TN
10. Schuh, C.A. 2016, “Stabilization of Nanostructure in Electrodeposits: From Theory to Commercialization”, European Union SELECTA Workshop, Dresden, Germany
11. Schuh, C.A. 2016, “Nanocrystalline Alloys Stabilized for Commercial Application”, OZ-16, The 9th International Symposium on Nanostructures, Wenden Germany
12. Schuh, C.A. 2016, “Nanocrystalline Alloys Stabilized for Commercial Application”, Materials Keynote, TechConnect World Innovation Conference, National Harbor, MD
13. Schuh, C.A. 2016, “Nanocrystals, Functional Grading, and ‘Suresh Gold Dust’”, Conference on Research,

Innovation and Leadership at the Crossroads of Science, Engineering and Medicine, Madrid, Spain
14. Schuh, C.A. 2016, "Grain Boundary Alloying in Nanocrystalline Metals in Theory and in Practice", Frontiers in Materials Sciences Lecture, Pacific Northwest National Laboratory, Pasco, WA
15. Schuh, C.A. 2016, "Stable Nanocrystalline Metals: Next-Generation Structural Materials from Science to Commercialization", Yale University, Department of Mechanical and Materials Engineering Seminar, New Haven CT
16. Schuh, C.A. 2016 "Stable Nanocrystalline Electrodeposits: Case Studies Spanning from Theory to Products", Electrochemical Society PRIME Meeting, Honolulu HI
17. Schuh, C.A. 2016, "Sintering in Nanocrystalline Alloys Favoring Grain Boundary Segregation and Second Phase Precipitation", Materials Science and Technology MS&T2016, Symposium on Sintering and Grain Growth, Salt Lake City, UT
18. Schuh, C.A. 2016, "Stable Nanocrystalline Metals: Next-Generation Structural Materials from Science to Commercialization", University of Pittsburgh, Department of Mechanical and Materials Science Seminar, Pittsburgh PA
19. Schuh, C.A. 2017, Van Horn Distinguished Lecture Series, Case Western Reserve University, Cleveland, OH: 1. "Harder, Cheaper, Greener: The Materials Science and Engineering of Nanostructured Metal Coatings", 2. "Materials Entrepreneurship: Nanostructured Metal Coatings as a Platform Technology", 3. "Materials Scale-Up Science: How Thermodynamics Enables Mass Manufacturing of Bulk Nanostructured Materials"
20. Schuh, C.A. 2017, "Stable Nanocrystalline Metals: Next-Generation Structural Materials from Science to Commercialization", City University of Hong Kong, Institute for Advanced Study, Distinguished Lecture Series, Hong Kong
21. Schuh, C.A. 2017, "Commercialization of Materials Technologies: Trends and a Case Study From MIT's Department of Materials Science and Engineering", MTEC National Metallurgy Laboratory Seminar, Bangkok, Thailand
22. Schuh, C.A. 2017, "Stable Nanocrystalline Metals: Next-Generation Structural Materials from Science to Commercialization", Boeing Metals and Materials Group, Everitt, WA
23. Schuh C.A. 2017, "Design of Stable Bulk Nanocrystalline Alloys", International Workshop on Multifunctional Structure at the Nanoscale, Duisburg, Germany
24. Schuh C.A. 2017, "How Grain Boundary Segregation Enables 3D Printing of Bulk Nanostructured Metals", Max Planck Institut für Eisenforschung 100th Anniversary Symposium, Düsseldorf, Germany
25. Schuh, C.A. 2017, "Nanostructure Stabilization by Grain Boundary Segregation: Challenges and Opportunities in Theory and Experiment", Symposium on Interfaces, Grain Boundaries and Surfaces from Atomistic and Macroscopic Approaches, MS&T2017, Pittsburgh, PA
26. Schuh, C.A. 2017, "The Inverse Problem in Atomistic Thermodynamics: A Method to find Element Combinations that Achieve a Target Atomistic Structure", Symposium on Advanced Atomistic Algorithms in Materials Science, Materials Research Society Fall Meeting, Boston MA
27. Schuh, C.A. 2017, "Nanostructure Configurations in Ternary Alloys", MRS Fall Meeting

RPPR Final Report
as of 12-Jun-2018

Honors and Awards: PI Awards during the project years 2014-2017: Christopher A. Schuh

Materials Research Society Outstanding Paper 2014
6th Morris E. Fine Lecture in MS&E, Northwestern University 2015
D.B. Robinson Distinguished Lecture, University of Alberta 2015
Howard K. Birnbaum Lecture, University of Illinois 2015
Fellow of the Minerals, Metals and Materials Society 2015
Van Horn Distinguished Lecturer, Case Western Reserve University 2017
Fellow of ASM International 2017

Graduate student awards on this project:

Tongjai Chookajorn:
-Outstanding Presentation Award, Young Scientists' Recommendation, 4th WMRIF Young Scientists Workshop 2014
-Best PhD Thesis Award, Department of Materials Science and Engineering, MIT 2014

Zachary Cordero:
-Graduate Student Teaching Award in Teaching a Graduate Subject 2015
-Best Poster Award (Tied), Materials Processing Center's Materials Day 2014

Michael Gibson:
-Best Poster Award, Gordon Research Conference on Frontiers in Physical Metallurgy 2015
-Graduate Student Teaching Award in Teaching a Graduate Subject 2015
-Best Poster Award (Tied, different poster), Materials Processing Center's Materials Day 2014
-NDSEG Fellowship 2013

Arvind Kalidindi:
-NDSEG Fellow 2015
-Lindau Award 2015

Protocol Activity Status:

Technology Transfer: Some of our research on nanocrystalline tungsten was conducted as part of a team of researchers from ARL including Brian Schuster, Emily Huskins, and Kris Darling has also produced a methodology for producing bulk W nanocrystalline metals with superior strength and ballistic properties. A variety of joint MIT-ARL publications have resulted from this work.

Our group also worked with researchers B.G. Clark, K. Hattar, M.T. Marshall, and B.L. Boyce from Sandia National laboratory to identify Fe alloys with predicted nanocrystalline stability. Sandia is pursuing the use of several of our alloys in DOE-specific niche applications in the Sandia mission.

Xtalic Corporation was founded by the PI a decade based on early ARO-funded research on nanocrystalline alloys. Xtalic licenses the technology for stabilization of electrodeposited nanocrystalline alloys developed under ARO support, is profitable, and remains privately held.

More recently (2015) the PI founded Veloxint Corporation, to commercialize the powder-route nanostructured alloys developed under current ARO support. The initial applications of interest for nanostructured W and Cr alloys are in the domain of masonry cutting tools and related industrial working tools. DOD-related applications may involve carbide replacement in high-density materials applications. Veloxint is funded by venture and strategic investors, employs almost 20 people and has a rapidly growing footprint in Massachusetts. Veloxint licenses all of the patents filed under the present program pertaining to powder metallurgy for nanocrystalline metals.

Finally, the research supported under this program is broadly shared with industry through interactions initiated between the PI and industry contacts. Research results have been shared with many companies through meetings with research scientists and executives, or through formal company seminars: NASA, Stanley Black and Decker, BAE Systems, ExxonMobil, 3M, Broad Group, Tata Steel, Maxion, Bosch, SNCF, Quimmco, Toyota, Boeing, Dyson, and others.

DISSERTATIONS:

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Nothing to report in the uploaded pdf (see accomplishments)