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7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
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14. ABSTRACT
This final report summarizes the findings of three years of research on the theory, design, and reduction to practice of nanocrystalline tungsten alloys with nanostructure sufficiently stable to envision a long time-at-temperature powder consolidation cycle. Theoretically, our work to develop the thermodynamics of nanostructured alloy systems presents a new concept to the field of solid-state science: a nanostructured solid solution that can be a ground state for the system. In a design sense, the concept can be used to screen possible alloying elements to

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Report Title

Thermodynamic Stabilization of Powder-Route Nanocrystalline Tungsten Alloys

ABSTRACT

This final report summarizes the findings of three years of research on the theory, design, and reduction to practice of nanocrystalline tungsten alloys with nanostructure sufficiently stable to envision a long time-at-temperature powder consolidation cycle. Theoretically, our work to develop the thermodynamics of nanostructured alloy systems presents a new concept to the field of solid-state science: a nanostructured solid solution that can be a ground state for the system. In a design sense, the concept can be used to screen possible alloying elements to down-select to the most promising for detailed study, and in the case of W, we identify Ti as a preferred alloying element for nanostructure stabilization. Experimentally, we have produced a variety of W alloys and evaluated their stability. In the W-Ti system we have verified stability over periods of many days at temperatures up into the consolidation range (~1100 C). Technologically, the combination of theory, design, and proof-of-concept demonstration offers a pathway for future alloy design in cases where nanostructuring is desirable for improved performance.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
04/03/2013	4.00	Timothy J. Rupert, Christopher A. Schuh. Mechanically driven grain boundary relaxation: a mechanism for cyclic hardening in nanocrystalline Ni, Philosophical Magazine Letters, (01 2012): 0. doi: 10.1080/09500839.2011.619507
04/03/2013	8.00	Timothy J. Rupert, Wenjun Cai, Christopher A. Schuh. Abrasive wear response of nanocrystalline Ni–W alloys across the Hall–Petchbreakdown, Wear, (02 2013): 0. doi: 10.1016/j.wear.2013.01.021
04/03/2013	7.00	Heather A. Murdoch, Christopher A. Schuh. Stability of binary nanocrystalline alloys against grain growth and phase separation, Acta Materialia, (04 2013): 0. doi: 10.1016/j.actamat.2012.12.033
04/03/2013	6.00	T. Chookajorn, H. A. Murdoch, C. A. Schuh. Design of Stable Nanocrystalline Alloys, Science, (08 2012): 0. doi: 10.1126/science.1224737
04/03/2013	5.00	Timothy J. Rupert, Jason R. Trelewicz, Christopher A. Schuh. Grain boundary relaxation strengthening of nanocrystalline Ni–W alloys, Journal of Materials Research, (03 2012): 0. doi: 10.1557/jmr.2012.55
08/30/2011	1.00	Christopher A. Schuh, Timothy J. Rupert. Sliding wear of nanocrystalline Ni–W: Structural evolution and the apparent breakdown of Archard scaling, Acta Materialia, (07 2010): 0. doi: 10.1016/j.actamat.2010.04.005
08/30/2011	2.00	Timothy J. Rupert, Jonathan C. Trenkle, Christopher A. Schuh. Enhanced solid solution effects on the strength of nanocrystalline alloys, Acta Materialia, (02 2011): 0. doi: 10.1016/j.actamat.2010.11.026
08/30/2011	3.00	Timothy J. Rupert, Christopher A. Schuh. Mechanically-driven grain boundary relaxation: a mechanism for cyclic hardening in nanocrystalline Ni, Philosophical Magazine Letters, (09 2011): 0. doi:

TOTAL: **8**

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received	Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

1. October 2009, “Grain Boundary Relaxation in Nanocrystalline Alloys and its Effect on Mechanical Properties”, Materials Science and Technology Annual Conference (ASM/TMS/ACerS), Symposium on Mechanical Properties and Grain Boundaries, Pittsburgh PA
2. January 2010, “Alloys with Grain Sizes Approaching the Amorphous Limit: Open Questions in Structure and Mechanical Properties”, Spallation Neutron Source VULCAN Commissioning Workshop, Oak Ridge National Laboratory, Oak Ridge, TN
3. March 2010, “Nanocrystalline Ni-W Alloy Coatings in Industrial Service”, Symposium on Nanostructured Materials, International Conference on Computational and Experimental Engineering Science, Las Vegas, NV
4. April 2010, “Achieving Control over Topological Disorder in Alloys”, National Research Council, Standing Committee on Condensed Matter and Materials Research, Washington DC
5. May 2010, “Design of Stabilized Nanocrystalline Metals”, Condensed Matter Theory Seminar, Harvard University, Cambridge, MA
6. September 2010, “Solute Distribution in Weakly Segregating Nanostructured Alloys”, 2010 Annual Risoe Symposium, Risoe National Laboratory for Sustainable Energy, Roskilde Denmark
7. October 2010, "Structural Evolution during Sliding Wear of Nanocrystalline Ni-W Alloys", 2010 MS&T Conference and Exhibition, Houston, TX.
8. November 2010, “Nanocrystalline Metals: Processing, Emerging Alloy Design Principles, Properties and Applications”, Tenaris University, Tenaris, Inc., “webinar” to locations in the US, Canada, Mexico, Argentia, Italy, and Romania
9. December 2010, "Separating Solid Solution and Grain Size Strengthening in Nanocrystalline Alloys" 2010 MRS Fall Meeting, Boston, MA.
10. January 2011, “Harder, Cheaper, Greener: the Materials Science and Engineering of Nanocrystalline Alloy Coatings”, McGill University, Department of Materials Science and Engineering Seminar, Montreal, Quebec, Canada
11. Also at Ohio State University, February 2011
12. Also at Arizona State University, April 2011
13. July 2011, “High Strength, Low Density, Ductility, and Strain Rate Hardening in Nanocrystalline Alloys”, International Conference on Materials for Advanced Technologies, Singapore
14. August 2011, “Design of Stable Nanostructure in Alloys: From Engineering Coatings to Extreme Specific Strength Sheet Metal”, Chulalongkorn University Institute of Metallurgical Research, Bangkok, Thailand
15. November 2011, “Design and Deployment of Stabilized Nanocrystalline Alloy Coatings”, Chinese Academy of Sciences, Institute for Metals Research, Shenyang, China
16. December 2011, “Advanced Materials From Research to Commercialization”, Apple Computer, Cupertino CA
17. January 2012, “Engineering Alloys: Ten Times Better. How Controlling the Grain Boundaries in Materials Can Improve Performance and Lower Cost”, MIT ILP-Japan Conference, Tokyo, Japan.
18. February 2012, “Harder, Cheaper, Greener: The Design and Deployment of Stabilized Nanocrystalline Alloy Coatings”, University of Illinois Materials Science and Engineering Seminar, Urbana, IL
19. Also at the 2012 Indo-American Frontiers of Engineering Symposium, Arlington VA, March 2012
20. Also at Rensselar Polytechnic Institute, Troy NY, April 2012
21. March 2012, “Design of a Nanocrystalline Alloy Coating for Electrical Connector Applications”, TMS Annual Meeting, Symposium on Materials Design Approaches and Experiences
22. July 2012, “Design and Deployment of Nanocrystalline Alloys with Grain Sizes Near the Amorphous Limit”, Chinese Academy of Sciences, Institute of Physics, Beijing, China
23. Also at Advanced Research Center of India, Hyderabad, India, August 2012
24. July 2012, “Engineering Alloys, Ten Times Better: How Grain Boundary Design can Improve Performance and Lower Cost”, Saint Gobain Research Center, Northborough, MA
25. Also at HC Starck, Inc., Newton MA, October 2012
26. August 2012, “Mechanics of Nanocrystalline Alloys with Grain Sizes Near the Amorphous Limit”, 16th International Conference on Strength of Materials, Bangalore, India
27. September 2012, “Harder, Cheaper, Greener: The Design and Deployment of Stabilized Nanocrystalline Alloy Coatings”, ASM International, Boston Chapter Seminar Series, Cambridge MA
28. Also at University of North Carolina, Department of Materials Science and Engineering Seminar, October 2012
29. Also at University of Connecticut, Department of Materials Science and Engineering, December 2012
30. September 2012, “The Multiscale Challenge of Metallic Glass Deformation”, Plenary Lecture, Materials Science and Engineering Congress, Darmstadt Germany
31. October 2012, “Grain Boundary Engineering for Materials with Enhanced Properties”, 2nd Annual Mechanical Engineering Technologies Conference, MIT Lincoln Laboratory, Lexington MA
32. November 2012, “Engineering Alloys, Ten Times Better: How Grain Boundary Design can Improve Performance and Lower Cost”, ILP Research Conference, Cambridge, MA
33. December 2013, “Design of Stable Nanocrystalline Alloys Using Grain Boundary Segregation”, Materials Research Society Annual Meeting, Boston MA

Number of Presentations: 33.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received		Paper
04/03/2013	9.00	Heather A. Murdoch, Christopher A. Schuh. Estimation of grain boundary segregation enthalpy and its role in stable nanocrystalline alloy design, Journal of Materials Research (03 2013)

TOTAL: 1

Number of Manuscripts:

Books

Received Paper

TOTAL:

Patents Submitted

STABLE BINARY NANOCRYSTALLINE ALLOYS AND METHODS OF IDENTIFYING SAME, H. Murdoch and C. A. Schuh, filed 2012 with US and PCT

Patents Awarded

Awards

1. S. Chandrashekar Young Investigator Award in Theory, Int'l Conf. on Computational and Experimental Engineering and Sciences,
2010, awarded to C. Schuh
2. Materials Research Society Outstanding Paper, 2010, awarded to C. Schuh and students
3. MIT MacVicar Faculty Fellow, 2011, awarded to C. Schuh
4. Ralph R. Teetor Educational Award, SAE International, 2011, awarded to C. Schuh
5. Lee Hsun Young Scientist Lecture in Materials Science, Chinese Academy of Sciences 2011, C. Schuh
6. NAE Indo-American Frontiers of Engineering, 2012, C. Schuh
7. Northwestern University Materials Science and Engineering Alumni Award 2012, C. Schuh
8. Japan Institute of Copper Best Paper Award 2012, C. Schuh

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Heather Murdoch	0.50	
Tongjai Chookajorn	1.00	
FTE Equivalent:	**1.50**	
Total Number:	**2**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Christopher A. Schuh	0.02	
FTE Equivalent:	**0.02**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	Discipline
Shaymus Hudson	1.00	Materials Science and Engineering
Amy Plunk	0.50	Materials Science and Engineering
Elizabeth Krueger	1.00	Materials Science and Engineering
FTE Equivalent:	**2.50**	
Total Number:	**3**	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 3.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 3.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 2.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 2.00

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The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME	
Total Number:	

Names of personnel receiving PHDs

NAME	
Timothy J. Rupert	
Heather A. Murdoch	
Total Number:	2

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

5 **STABLE BINARY NANOCRYSTALLINE ALLOYS AND METHODS OF IDENTIFYING SAME**

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) Y

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2): PCT

5a: Heather A. Murdoch

5f-1a: MIT

5f-c: 77 Massachusetts Avenue

Cambridge MA 02139

5a: Christopher A. Schuh

5f-1a: MIT

5f-c: 77 Massachusetts Avenue

Cambridge MA 02139

Scientific Progress

The goal of this project is to develop a tungsten-rich alloy powder that can be produced readily in a nanocrystalline form, and which is sufficiently stable to resist significant structural change during high-temperature consolidation to full density. To achieve this goal we employ both theoretical modeling, to identify candidate alloys with improved stability in the nanocrystalline state, and experimentation, to produce and test alloy powders and validate the model.

Theoretical

The Regular Nanocrystalline Solution (RNS) model, developed under ARO funding in previous work by the PI, predicts the existence of a nanocrystalline phase that is stable against grain growth via grain boundary segregation. The existence of a segregation state that reduces the grain boundary energy to zero depends on the materials properties (encapsulated in the enthalpy of mixing and the enthalpy of segregation for the binary alloy) and composition ranges.

A second consideration for the stability of a nanocrystalline alloy is its stability against second phase precipitation. Many existing nanocrystalline alloys (such as Ni-W, Ni-P, Co-P, and others) have stable nanostructures until a second phase precipitates and disrupts the segregation state required for grain size stability. In order to quantify the stability of a nanocrystalline binary alloy with respect to second phase formation, we compare the Gibbs free energy of the predicted (from RNS) stable NC phases to the free energy of secondary phases.

Varying the materials parameters in the RNS model across the range of appropriate values, we have produced a nanocrystalline behavior map with three regions, one where there is no NC phase that is stable in the particular system, one in which a NC phase exists that is stable against grain growth but not phase separation, and one in which the NC phase that exists is stable against both grain growth and phase separation. To our knowledge, we were the first group to propose that a GB-segregated nanocrystalline solid solution can actually be a ground state for an alloy system. This calls for re-evaluation of "equilibrium" phase diagrams that do not consider such states, and suggests that there may be a multitude of stable nanocrystalline alloy systems waiting to be discovered.

The suitability of tungsten based alloys was evaluated at first pass using nanocrystalline stability maps. The property space examined by the RNS model involves only binary alloys with positive enthalpies of mixing, denoting phase separating materials. From this short list, we selected W-Ti and W-Cr as the most promising binary systems. (Problems with the other systems include much lower melting points than powder consolidation temperatures, expense, and a narrow composition range over which NC phases exist.)

We also used the RNS model to predict a number of additional, unexpected new ground states with nanoscale structures. These include systems with stable amorphous structures, duplex nanostructures, and bimodal structures. We hope to continue to explore these possible structures in future work.

Experimental Program

Our work has focused heavily on W-Ti alloys. This system is one that consistently emerges from our theoretical work as a preferred option for stabilization of nanocrystalline W; the Ti additive is introduced because it has a low tendency to phase separate, but can segregate to grain boundaries and lead to nanostructure stabilization. Alloys have been processed by ball milling with the W content ranging from 80 to 100 at% W or from 94 to 100 wt% W. The powders were mechanically alloyed in a SPEX 8000 high-energy ball mill, using a tungsten carbide vial and tungsten carbide balls.

We explored the structural stability of W-Ti alloys at several different compositions levels (0, 1, 2, 5, 10, and 20% Ti), using a variety of tools including x-ray diffraction (at ambient and elevated temperature up to 1200 C), transmission electron microscopy (TEM), scanning TEM, etc. The average grain size of tungsten after milling and before thermal exposure was found to be between 16 and 21 nm. In pure tungsten, the grains grow significantly to an average size of 180 nm after annealing at 950 C for 4.5 hours. On the other hand, a small addition of solutes helps suppress grain coarsening. The average grain size after annealing at 1000 C for 4.5 hours for a sample with a higher solute loading of 6 wt% was 23 nm. With a lower solute loading level (~1-2 wt%), the stability is reduced, although still better than pure tungsten (grain growth to 110 nm for the same treatment at 1000 C).

The extent of thermal stability of tungsten alloys was further analyzed through long-time anneals at relevant powder consolidation temperatures. For example, the alloy with 6 wt% solute concentration was annealed at 1000 C for two weeks and the grain size estimated from X-ray diffraction was found to still be below 30 nm. At 20% Ti, we found near ideal stability at 1100 C for over a week. We also confirmed that in this alloy the chemical configuration is nonuniform as expected for a nano-system.

These results on W-Ti alloys conform to the expectations of our theoretical work, and experiments on the consolidation of these alloys at modest temperatures (below 1500 C) are now underway.

Technology Transfer

The PI has a long history of successful technology transfer, and in the present case the filing of one patent and the imminent filing of a second present pathways to interaction with commercial partners. The PI has delivered lectures on the funded work to numerous industrial concerns, including some that would be natural commercialization partners.

Another main technology transfer emerging from this work is the hiring of the PI’s senior graduate student, Heather Murdoch, at ARL; as she transitions from MIT to ARL, Dr. Murdoch will carry her leading-edge knowledge of nanocrystalline alloy design directly to the Army.

Technology Transfer