Final Report

Project Title: Strengthening Nanotwinned Metals beyond the Hall-Petch Limit

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<tr><td colspan="2">Federal Award Identification Number: DE-SC0016270</td></tr>
<tr><td colspan="2">Organization: Office of Basic Energy Sciences, DOE EPSCoR</td></tr>
<tr><td>Project Period: 08/15/2016 - 08/14/2019</td><td>Report Date: 11/14/2019</td></tr>
<tr><td>Budget: $586,000</td><td></td></tr>
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<tr><td>Participating National Laboratories:
Lawrence Livermore National Laboratory
Ames Laboratory</td><td></td></tr>
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Abstract:

A research partnership program was conducted to study the roles of trace element segregation as a fundamentally new mechanism of grain-boundary and twin-boundary strengthening in nanocrystalline-nanotwinned face-centered-cubic silver metals. The goals were to create new metals that break the decades-old theoretical Hall-Petch strength limit, and to study a new class of super-strong conducting materials. This program combined synergistic experimental and computational studies at the atomic scale, using a wide range of resources and scientific expertise at the University of Vermont, Ames Laboratory and Lawrence Livermore National Laboratory. This research led to a discovery that annealing of nanotwinned silver with trace concentrations of Cu solute atoms (<1.0 wt.%) results in grain sizes and twin spacings well below those previously obtained for silver. These new materials, termed as nanocrystalline-nanotwinned silver, showed a record hardness 42% higher than the Hall-Petch limit in pure nanotwinned silver or stronger metals like copper, with excellent retention of electrical conductivity and microstructure stability at elevated temperature. This research used large-scale hybrid Monte-Carlo/molecular-dynamics atomistic simulations and ab-initio calculations to predict new impurity-segregation behaviors and fundamentally new plastic deformation mechanisms in nanocrystalline-nanotwinned silver metals. A new interatomic potential for atomistic simulation of segregation of Ni impurity in Ag grain-boundaries and plasticity of Ag-Ni alloys was developed.

I. ACCOMPLISHMENTS

I.A. What are the major goals of the project?

The specific goals of this partnership program were three-fold:

(1) To use hybrid Monte-Carlo/molecular-dynamics (MC/MD) atomistic simulations and density-functional-theory (DFT) based ab-initio calculations to study the effects of nanotwin-size, grain-size and solute atom segregation on strength and associated plasticity mechanisms in nanocrystalline-nanotwinned Ag metals.

(2) To develop new theories for predicting how different impurity elements (Cu, Ni and Al) addition influence grain-boundary segregation and strengthening mechanisms in nanocrystalline-nanotwinned metals.

(3) To integrate computational simulations, theory, and experiments at the atomic scale for rapid prototyping of new metallic alloys with exceptional combination of strength, stability and electrical conductivity.

I.B. What are the key outcomes and accomplishments under these goals?

Outcome 1 – A new theory for softening and maximum strength in nanotwinned metals: In this project, it was discovered that nanocrystalline-nanotwinned Ag metals exhibit two strength transitions dissimilar from the previously known mechanisms. Atomistic simulations showed three distinct strength regions as twin spacing decreases, delineated by positive Hall-Petch strengthening to grain-boundary-dictated (near-zero Hall-Petch slope) mechanisms, and to softening (negative Hall-Petch slope) induced by twin-boundary (TB) defects (Fig. 1a,b). We have developed a new predictive theory of defect-induced softening in nanotwinned metals (Fig. 1c,d). Also, an ideal maximum strength without softening was found for a range of TB spacings below 7 nm with perfect TBs (Fig. 2c).

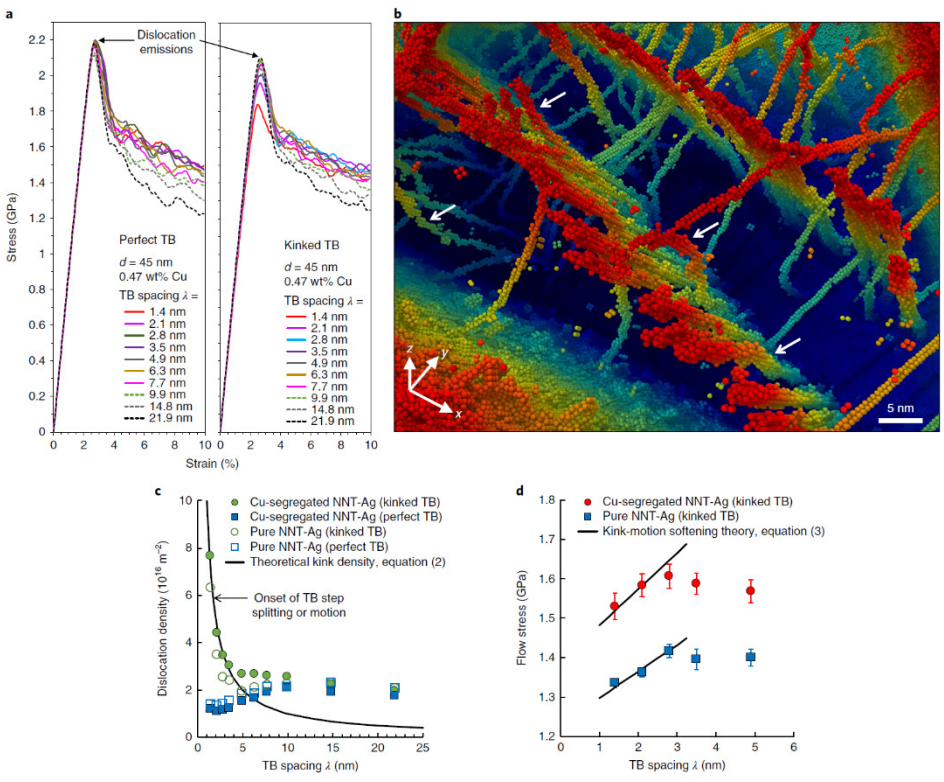

Figure 1. Twin-boundary defect-motion softening mechanism (negative HP slope). a. Simulated stress-strain curves for different twin spacings λ for both kinked and perfect twin boundaries in Cu-mixed Ag with a grain size d= 45 nm. The onset of dislocation nucleation mechanisms is shown by an arrow at the peak of stress. **b.** Atomistic deformation snapshot at 5% strain inside a grain containing kinked twin boundaries when λ = 1.4 nm. All face-centered cubic atoms have been removed for clarity. The arrows indicate partial dislocations from splitting or motion of twin-boundary kink steps that are responsible for the softening behavior. **c.** Density of Shockley partial dislocations at 5% applied strain, as a function of λ. The solid line represents a theoretical estimate of the initial kink density showing that the dislocation density is dominated by kink motion when λ < 3.5 nm. **d.** Comparison of plastic flow stresses predicted by MD and theoretical model for kink-motion softening. (from Ke et al. *Nature Materials* 2019)

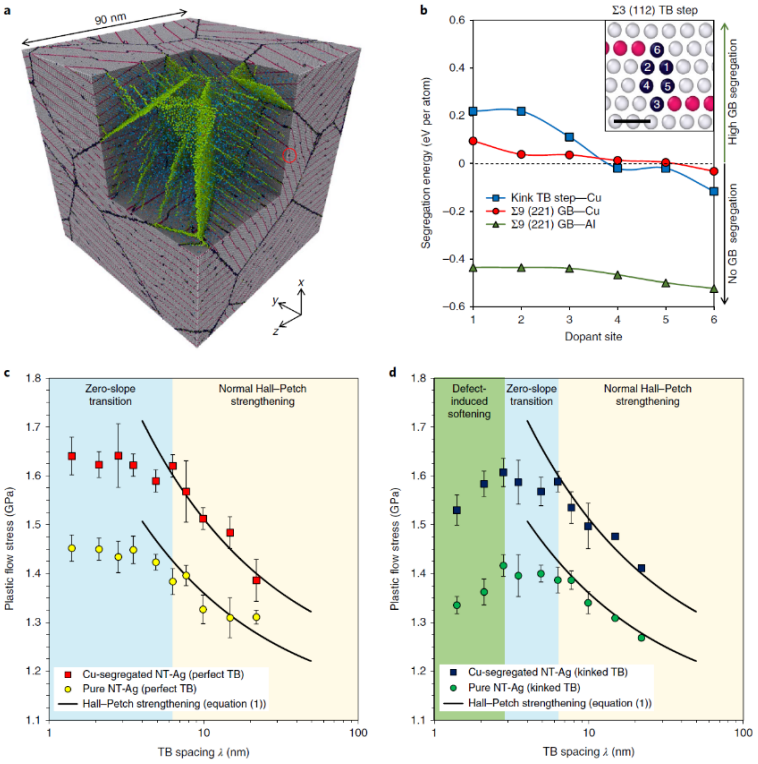

Figure 2. Hall-Petch strength transition zones in pure and impurity-segregated nanotwinned Ag metals containing either perfect or kinked twin boundaries (TBs) obtained by large-scale atomistic simulations. a. Snapshot of hybrid Monte-Carlo and molecular dynamics simulation of microstructure relaxation and equilibrium impurity segregation after 500 K annealing in nt-Ag with a target concentration of 0.47 wt.% Cu, λ = 3.5 nm and d = 45 nm. First, common neighbor analysis is performed to differentiate atoms from coherent TBs (magenta color), incoherent interface defects (dark purple), and face-centered cubic (FCC) atoms (light grey). Second, Ag atoms are removed from one of the corner regions to highlight its Cu impurity distribution. In this region, Cu atoms are colored in green, dark purple and blue when found at incoherent interfaces, coherent TBs and FCC lattice, respectively. Red circle highlights an internal TB kink-step defect added to the atomistic model. **b.** First-principles density-functional-theory calculations of the six highest substitutional segregation energies at different local sites of a twin-boundary kink step and a high-energy Σ9 (211) tilt grain boundary, respectively. Sites 1-6 of the kink defect are indicated in inset. Scale bar is 0.5 nm. Hall-Petch flow strength plots for pure and Cu-segregated nt-Ag with **c.** perfect coherent TBs and **d.** kinked TBs. (from Ke et al. *Nature Materials* 2019)

Outcome 2 – **Quantifying grain-boundary segregation effects on plasticity of nanocrystalline-nanotwinned Cu-mixed Ag metals.** A series of large-scale hybrid MC/MD simulations containing up to 42 million atoms each has been performed to simulate the annealing and plastic deformation of Ag with 10 different twin spacings (1.4 – 22 nm), 8 grain sizes (6 – 45 nm) and a range of impurity concentrations (0 – 15 at% Cu). Our atomistic simulations revealed that Cu impurity segregation prompts an impressive interface-strengthening effect that saturates at a concentration of 8 at.% due to a mechanism transition from GB-controlled plasticity to localized shear banding (Fig. 3c-e). We found the critical Cu concentration promoting strengthening up to the ideal Hall-Petch limit as shown in Fig. 3f.

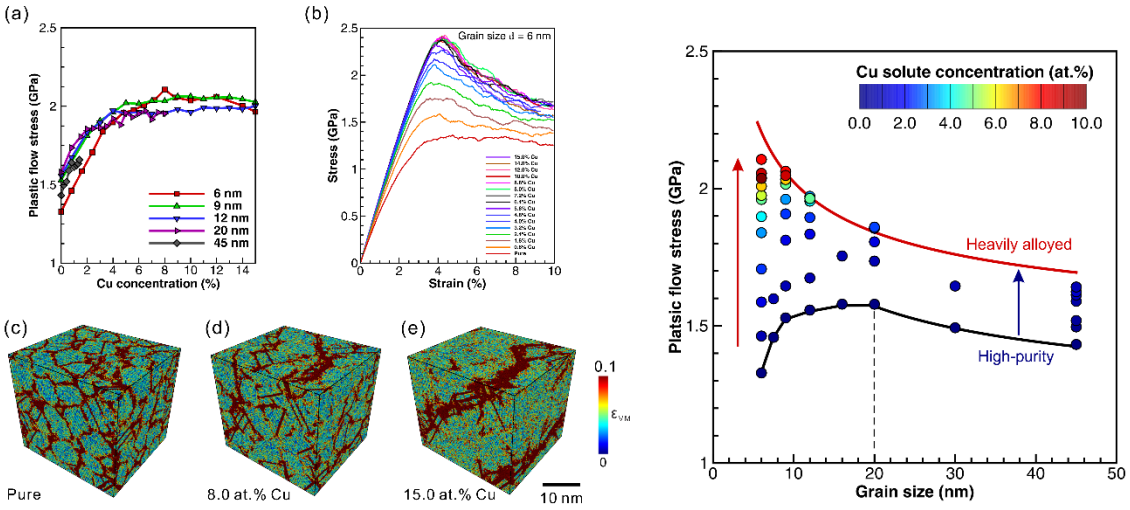

Figure 3. Segregation strengthening as a function of grain size in nanocrystalline Ag-Cu alloys. Influence of segregated Cu concentration on **(a)** plastic flow stresses and **(b)** stress-strain curves at a 6-nm grain size. **(c)-(e)** Deformation mechanism transition for GB-mediated to shear banding as Cu concentration increases. **(f)** Critical Cu concentration leading to strengthening at the ideal Hall-Petch limit.

Outcome 3 – **Understanding segregation effects on twin stability in nanocrystalline-nanotwinned Cu-mixed Ag**

It was found that solute Cu atoms segregate concurrently to grain boundaries and intrinsic kink-like twin boundary defects during thermal annealing (Fig. 4). Low Cu impurity contents below 1 at. % were predicted to substantially increase twin stability in nanotwinned Ag, accompanied with a pronounced rise in yield strength. Incipient plasticity is associated with kink-step migration, grain-boundary sliding, and dislocation nucleation from grain boundaries and twin-boundary defects, which are affected by doping. Cu-dependent yield strengthening in doped nanotwinned Ag is shown to correlate with the critical stress required to initiate crystal slip emitted from grain boundaries and twin-boundary defects. These findings provide fundamental insight into the roles of twin-boundary imperfections on plastic yielding and offer new clues to extend the stability of nanotwinned metals by microalloying.

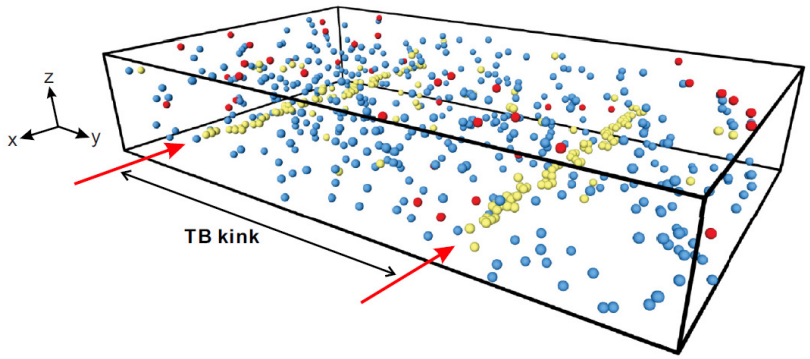

Figure 4. Hybrid MC/MD simulations of segregation of 0.8 at. % Cu atoms in nanotwinned Ag during 500 K annealing. Cu atom distribution after segregation in GB-free bicrystal model containing one twin-boundary (TB) kink defect. Cu atoms segregated to TB kink steps and GBs are colored in yellow, those moved to coherent TB segments in red, and other atoms staying in solution are in blue color. The original position of individual TB kink steps was indicated with a red arrow. (from Ke et al. *Physical Review Materials* 2017)

Outcome 4 - **Development a new EAM interatomic potential for segregation and plasticity in Ag-Ni alloys**

1. **A new ab-initio database.** The software VASP was used to perform ab-initio MD to simulate single crystal, bicrystal and liquid structures in Ag and Ni20Ag80, and geometry optimization to achieve the minimum potential energy of various configurations. Only Σ point calculation was carried out due to the relatively large simulation cell used. A 350eV-cutoff energy of the plane wave basis sets was used to expand Kohn-Sham orbitals. The exchange-correlation functional was PBE developed based on generalized gradient approximation (GGA) scheme. The interaction between ions and electrons was described using the projector augmented wavefunction method (PAW) pseudopotentials.
2. **A new Finnis-Sinclair Embedded-atom-method potential for simulating Ni impurity segregation in Ag interfaces.** The interaction between Ag atoms was modeled with a new potential developed by the PI and his collaborator (Dr. M. Mendelev at Ames Lab.) to correctly reproduce the Ag liquid structure and the stable and unstable stacking-fault-energies (SFEs), with a fitting database retrieved from our ab-initio calculations, while the interaction between Ni atoms is described with a potential taken from the literature. The cross potential used to describe the interaction between Ag and Ni atoms was fitted based on ab-initio data of 80Ag-20Ni liquid structure, vacancy formation energy in fcc AgNi alloy, segregation energy of Ni at different sites of a Σ9 (221) GB in Ag, and cluster formation energy of Ni in both Ag single crystal and Σ9 (221) GB. Additionally, the energy of a Σ3(112) TB kink step was included.

This new Ag-Ni potential not only reproduces properties included in the potential fitting, but also was able to predict some unique Ni segregation behaviors at interfaces, such as impurity clustering, in hybrid MC/MD simulations. Such a behavior is different from that predicted by Cu segregation, and therefore has been considered to play an important role on the Hall-Petch limits and associated plastic deformation mechanisms, as discussed below.

Outcome 5 – Discovery of heterogeneous versus homogeneous segregation behaviors with different types of impurities in Ag grain boundaries. Solute atom segregation energies to Σ9 (221) GB and kink (112) defect in Ag have been obtained using VASP calculations for three dopants, Ni, Cu and Al (Fig. 2b). Our ab-initio study suggested that Ni solute segregation to grain-boundaries and TB defects is more strongly favored than Cu solute segregation, while Al segregation was predicted to be weak. Surprisingly, our atomistic simulations have predicted that GB segregation behavior in nanocrystalline Ag alloys containing small Ni contents (≤ 2 at%) is intrinsically *heterogeneous*. Heterogeneous segregation is a unique behavior where solute atoms cluster along some interfaces, whereas other grain-boundary regions are left solute-free. Yet our basic understanding of this phenomenon remains limited, because common nanocrystalline alloys studied in the literature, such as Ag-Cu alloys, exhibit *homogeneous* segregation, with solutes atoms distributing uniformly along interfaces at all concentrations. Therefore, we hypothesize that new shear localization and ductility enhancement mechanisms induced by heterogeneous GB segregation could be controlled by the segregated solute content.

Outcome 6 – Impurity-mixed nanocrystalline-nanotwinned Ag metals with record strength, stability and electrical conductivity. Using magnetron sputter deposition, we have synthesized nanocrystalline-nanotwinned Ag with hardness 3.05 GPa — 42% higher than the current record, by segregating trace concentrations of Cu impurity (<1.0 wt.%). The microalloy retained excellent electrical conductivity and remained stable up to 653 K; 215 K better than for pure nanotwinned Ag. The normalized strength (σ_y/μ) of our nnt-Ag metals well surpassed those reported in various nanostructured metals and alloys with similar electrical conductivities. This exceptional combination of strength and electrical conductivity was far outside the inversely correlated strength-electrical conductivity zone typically seen in other metallic materials.

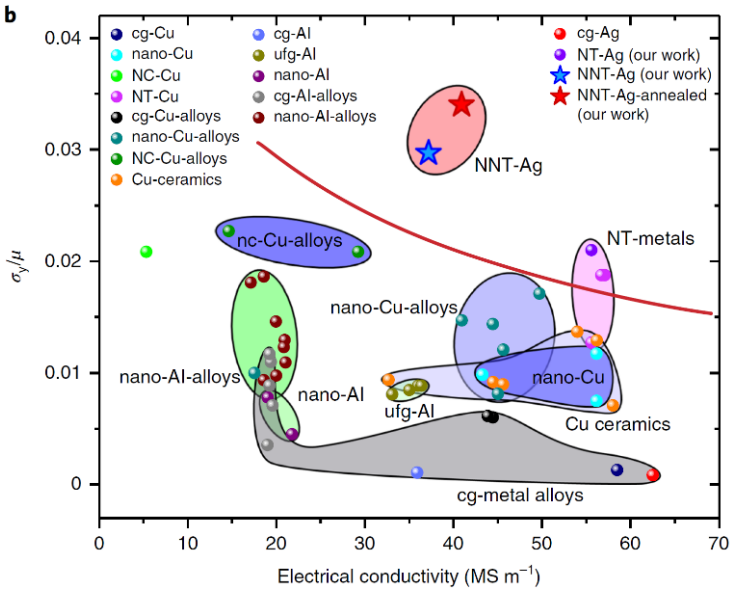

Figure. 5. Electrical conductivity and yield strength of Cu-impurity-mixed nanocrystalline-nanotwinned (NNT) Ag. A summary of yield strength/shear modulus (σ_y/μ) versus electrical conductivity of various metals and alloys, including nnt-Ag (our work where $\sigma_y = H/3$ with H the nanoindentation hardness), pure nt-metals, nanostructured Cu (nano-Cu), nano-Cu-alloys, ufg-Al, nano-Al, nano-Al-alloys, Cu-ceramics composites, and conventional commercial Cu alloys. The exceptional combination of strength and electrical conductivity in NNT-Ag exceeds that of existing materials, including the current benchmark nt-metals. The solid red line is a guide for the eye only.

I.C. What is the impact of the project?

This research studied a fundamentally new mechanism of grain-boundary and twin-boundary strengthening in nanotwinned metals, that could dramatically enhance the strength limits previously reached in face-centered-cubic metals and alloys. This new class of metals is relevant for extreme environments in structural applications.

This project used synergistic experimental and computational studies that collectively demonstrate that selective impurity segregation is a viable approach to creating super-strong nanostructured Ag metals, in concurrence with excellent electrical properties and high thermal stability. These new metallic materials are of potential interest for energy applications as transparent conductive electrodes for touchscreens and solar cells, catalysts, and plasmonic

materials. Our approach has certain advantages over existing heavy alloying and hierarchical interface-design strategies that may inevitably lead to the trade-off of other functional properties, such as the electrical conductivity.

The project made extensive use of DOE's new supercomputer Cori for large-scale atomistic simulations and ab-initio calculations. Combined computational and experimental efforts were powerful tools to identify these new materials.

I.D. What opportunities for training and professional development has the project provided?

This project has provided training to 1 undergraduate student, 2 PhD students and 1 postdoctoral fellow through one-on-one mentorship, as well as a course development on Multiscale Modeling given by the PI. 1 PhD student (Xing Ke) has presented a poster at the 2017 Fall Materials Research Society (MRS) meeting in Boston, MA. This poster has earned a nomination for best poster award. This student has also successfully defended his doctoral thesis in November 2018 and has presented an oral presentation at the 2018 MS&T conference in Columbus, OH. Also, the postdoctoral researcher, Dr. Zhiliang Pan, has given an invited oral presentation at the 18th International Conference on the Strength of Materials (ICSMA 18) at the Ohio State University in Columbus, OH. Undergraduate student Eve-Audrey Picard was the recipient of a competitive UVM Barrett summer research scholarship in 2019.

I.E. How have the results been disseminated to communities of interest?

Dissemination of the results produced during this project have been presented at invited seminars, conference talks, poster presentations and peer-reviewed journal publications, as shown in the Products section below.

II. PRODUCTS

II.A. Published Journal Articles

1. Xing Ke and Frederic Sansoz, "Segregation-affected Yielding and Stability in Nanotwinned Silver by Microalloying", ***Physical Review Materials*** 1, 063604 (2017)
2. Zhiliang Pan, Valery Borovikov, Mikhail I. Mendelev and Frederic Sansoz, "Development of a Semi-empirical Potential for Simulation of Ni Solute Segregation into Grain Boundaries in Ag", ***Modelling and Simulation in Materials Science and Engineering***, 26, 075004 (2018)
3. Jiangwei Wang, Guang Cao, Ze Zhang, Frederic Sansoz, "Size-dependent Dislocation-twin Interactions", ***Nanoscale*** 11, 12672-12679 (2019)
4. Xing Ke, Jianchao Ye, Zhiliang Pan, Jie Geng, Matt F Besser, Dongxia Qu, Alfredo Caro, Jaime Marian, Ryan T Ott, Y Morris Wang, Frederic Sansoz, "Ideal Maximum Strengths and Defect-induced Softening in Nanocrystalline-Nanotwinned Metals", ***Nature Materials*** 18, 1207–1214 (2019)

II.B. Other Publications

1. Xing Ke. Atomistic Simulation Studies of Grain-Boundary Segregation and Strengthening Mechanisms in Nanocrystalline Nanotwinned Silver-Copper Alloys. ***PhD Thesis, University of Vermont*** (2018)
2. Xing Ke, Frederic Sansoz, "Grain-boundary Segregation Strengthening beyond the Hall-Petch Limit in Nanocrystalline Ag-Cu Alloys". In preparation.
3. Zhiliang Pan, Frederic Sansoz, "Heterogeneous Segregation Suppresses Strain Localization in Nanocrystalline Alloys". In preparation.

II.C. Conference Abstracts and Presentations

1. Xing Ke, Frederic Sansoz, Yinmin M. Wang, Ryan Ott, Jaime Marian. Mechanical Properties of Nanocrystalline-Nanotwinned Silver Strengthened by Copper Impurity Segregation. Abstract for

Symposium "Deformation and Transitions at Grain Boundaries VI", **Materials Science & Technology 2018** conference - Columbus, Ohio

2. Zhiliang Pan, Xing Ke, Qiongjiali Fang, Frederic Sansoz. Segregation-mediated Strengthening Mechanisms in Nanotwinned Metals. Abstract for the **18th International Conference on the Strength of Materials**

3. Frederic Sansoz (invited speaker), "Small-scale Mechanics of Super-strong Silver Nanostructures", **2018 European MRS Spring Meeting**, Strasbourg, France (June 2018). Symposium AA— Strength, plasticity, fracture and fatigue behaviour controlled by interfaces and grain boundaries
4. F. Sansoz, "Small-scale Mechanics of Super-strong Silver Nanostructures", **Materials Science and Engineering Department Seminar**, **University of Connecticut**, seminar speaker (April 2018)
5. Frederic Sansoz (invited speaker), "Exploring the Limit of Strength in Nanocrystalline-Nanotwinned Silver", **2018 MRS Spring Meeting**, Phoenix, AZ (April 2018). Symposium NM10—Nano-Metallic Materials by Design
6. X. Ke and F. Sansoz: Copper Segregation Affected Yielding in Nanotwinned Silver, **2017 MRS Fall Meeting**, in Symposium PM3—Interfaces and Interface Engineering in Inorganic Materials, Boston, MA (November 2017). **Nominee for best poster award**
7. Frederic Sansoz (invited speaker), "Small-scale Mechanics of Nanoscale Materials", **University of Vermont College of Engineering and Mathematics' Board of Advisors Spring meeting** (April 2017).
8. Frederic Sansoz (invited speaker), Xing Ke, Qiongjiali Fang, "Intrinsic Twin Boundary Defects and Strength in Nanotwinned Ag and Ag-Cu Alloys", **2017 TMS Annual Meeting**, San Diego, CA (February 2017).
9. Frederic Sansoz (invited seminar), "Small-scale Mechanics of Nanoscale Metals", Jones Seminar at **Dartmouth College's Thayer School of Engineering**, (January 2017). Video available online on YouTube.com from https://www.youtube.com/watch?v=bMUZH9lVZ_w

10. Frederic Sansoz (invited speaker), "Enabling Superplastic Extensibility in Silver Nanocrystals at Room Temperature**", University of Vermont's ANGEL Workshop** (October 2016).

III. PARTICIPANTS & OTHER COLLABORATING ORGANIZATIONS

III.1. Participants

1) Name: **Frederic Sansoz (frederic.sansoz@uvm.edu)**

2) Project Role: PI

3) Support from this award: 3 summer months.

4) Contribution to Project: Prof. Sansoz has conducted research, wrote papers, mentor students and disseminated the results at seminars and conferences.

1) Name: **Xing Ke (xke@outlook.com)**

2) Project Role: Graduate Student

3) Support from this award: Full

4) Contribution to Project: Mr. Ke has performed work in the area of hybrid MC/MD simulations of Cu-mixed Ag alloy system.

1) Name: **Qiongjiali Fang (qfang1@uvm.edu)**

2) Project Role: Graduate Student

3) Support from this award: Partial (50%)

4) Contribution to Project: Ms. Fang has performed work in the areas of finite-element analysis and atomistic simulations of GB-controlled stress concentrations in nanotwinned metals.

1) Name: **Zhiliang Pan (zhiliang.pan@uvm.edu)**

2) Project Role: Postdoctoral Fellow

3) Support from this award: Full

4) Contribution to Project: Dr. Pan has performed work in the area of EAM potential development, ab-initio calculations using the software VASP, and hybrid MC/MD simulations for the Ni-mixed Ag alloy system.

1) Name: **Eve-Audrey Picard (Eve-Audrey.Picard@uvm.edu)**

2) Project Role: Undergraduate Student

3) Support from this award: Partial (only for equipment and materials support)

4) Contribution to Project: Ms. Picard developed an electrochemical setup during a summer internship to produce Ag-mixed nanocrystalline Ni alloys. She has also performed tensile testing on the synthesized specimens.

III.2. National Laboratory Partners

1) Organization Name: **Ames Laboratory**

2) Location of Organization: Ames, Iowa

3) Partner's contribution to the project: Dr. Ryan Ott has performed in-situ XRD heating analysis and materials synthesis. Dr. Mikhail Mendelev has performed the fitting of EAM potentials and provided guidance to the postdoctoral researcher in the ab-initio database development. Monthly emails or phone calls. In-person meeting at the 2017 TMS conference.

1) Organization Name: **Lawrence Livermore National Laboratory**

2) Location of Organization: Livermore, California

3) Partner's contribution to the project: Dr. Yinmin "Morris" Wang performed nanoindentation experiments and TEM analysis of specimens developed by Ames. Dr. Wang has also been directly involved in the discussion of simulation results and writing of articles with the PI. Weekly emails or phone calls. In-person meetings at the 2017 TMS conference.

1) Organization Name: **National Energy Research Scientific Computing Center (NERSC)**

2) Location of Organization: Berkeley, California

3) Partner's contribution to the project: Massively-parallel computational resources using Cori supercomputer

IV. Current and Pending Support

Role	PI and co-PIs list	Title of grant	Funding Agency	Total Amount	Status	Award Period
Co-PI	PI: M. White Co-PIs: Headrick, Sansoz, Landry, Webb	MRI: Acquisition of a Variable Pressure Field-Emission Scanning Electron Microscope for STEM Research and Education	NSF	$480,000 (direct only)	Funded	10/01/2018 to 09/30/2021
PI	Sansoz	Heat Conduction in Flexible 2-D Woven Ceramic Fibers for Extreme Atmospheric-entry Environments	VT NASA EPSCoR	$24,983 (no F&A)	Funded	08/01/2018 to 09/30/2019
PI	Sansoz	Role of Heterogeneous Segregation on Shear Localization Mechanisms in Nanocrystalline Alloys	DOE/BES	$584,936	Funded	08/15/2019 to 08/14/2022

V. Cost Status

Approved budget = $586,000.00

Actual cost incurred = $579,704.63

No cost-sharing