REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	**2. REPORT TYPE**	**3. DATES COVERED** *(From - To)*
10/07/2019	Final	09/15/2015-04/15/2019

4. TITLE AND SUBTITLE
Final Report: New Strategies in Alloy Development

5a. CONTRACT NUMBER
W911NF-15-2-0105

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Mark A Atwater

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Millersville University
1 S. George St
Millersville, PA, 17551

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release: distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			**19b. TELEPHONE NUMBER** *(include area code)*

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

Millersville University

P.O. Box 1002
Millersville, PA 17551-0302
www.millersville.edu

Department of Applied Engineering, Safety & Technology
Phone: 717-871-7237
Fax: 717-871-7931

Date: 6/28/2019
From: Mark Atwater
To: Kris Darling
RE: Final Report for Agreement #W911NF-15-2-0105

Dear Dr. Darling,

In accordance with our cooperative agreement, I am submitting this final report. As we have maintained regular contact throughout the performance of this project, I will highlight the accomplishments and their impacts. The opportunities to use and develop far from equilibrium materials continues to hold great promise, and I hope we can continue to work together in the future. The importance of our work is not limited to the creation of far from equilibrium materials, but we have also developed new strategies to prepare and study these vital materials. I expect those advancements to serve as a foundation for future development and to provide lasting value to the field.

1 New Strategies in Alloy Development

1.1 Cryogenic Processing

The advancements during this agreement include developing more reliable strategies for high-energy cryogenic ball milling. This effort reevaluated the design of these custom machines, and we worked through several iterations to create a fully enclosed environment, which not only allows the safe evacuation of gaseous nitrogen, it also allows the temperature in that environment to be controlled. Furthermore, it provides a protective atmosphere, which can be generated from the gaseous nitrogen or purged by means of separate valving. This allows room temperature milling to be performed in an inert atmosphere without requiring a more expensive glovebox. Perhaps most importantly, the redesign of the liquid nitrogen tubing to the vial has reduced the tendency for breakage, which has historically been one of the key challenges in this method. By positioning it lower on the milling arm, the amplitude of movement has been significantly reduced and stress on the tubing has been lowered as a result. Images of this setup are provided below.

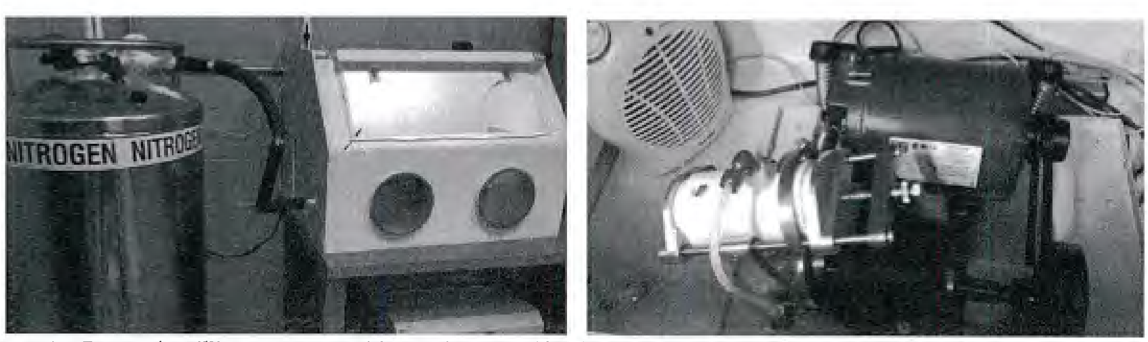

Figure 1 - Cryogenic milling apparatus with associated modifications to improve operational reliability and processing control.

1.2 *Cryogenic Testing*

In a related design, we also delivered to you a custom enclosure to perform microindentation tests at cryogenic temperature. This is of interest to characterize changes in mechanical properties at low temperatures. This design uses a standard microdindeter to be placed within the enclosure, and the atmosphere to be purged of air by inert gas. Once the moisture reading drops to an acceptable value, liquid nitrogen is flowed through a cold trap to condense any remaining moisture. To prevent the enclosure temperature from becoming excessively cold, a separate heating element is included. This allows for full slow of liquid nitrogen while maintaining a comfortable working environment. By opening a separate valve, the custom-made stage can be cooled, which is read by a separate thermocouple. Throttling the liquid nitrogen allows the stage temperature to be controlled. We demonstrated this setup on molybdenum foil, and images are included below.

Figure 2 - Cryogenic microindentation apparatus developed for low-temperature testing of materials properties.

1.3 *Linear Ball Mill*

Another development in processing achieved was the design and fabrication of a linear ball mill. This mill removes process variables, allows for the adjustment of milling energy, and it provides the framework for future modifications. Of particular challenge in this milling scheme is balancing the reciprocal energy my rotating mass. A counterweighted crank was utilized to achieve this, but in most designs where this type of setup is used (e.g., engines) the mass is minimized for optimum performance. This leads to practical limitations to the rotation rate at the crank. Therefore, we have primarily operated this initial incarnation at lower speeds (less than 6 Hz). This does not prevent higher speeds from being achieved in the future, but based on the motor, frame, and other physical factors, it is expected to be safest. This particular design, even though not optimized, has already proven valuable. In particular, by utilizing a custom insert for a standard SPEX milling vial, we have been able to control ball impact locality and correlate the milling energy to deformation. These early developments rely on the linear motion of this mill. Images demonstrating the design and use are provided below.

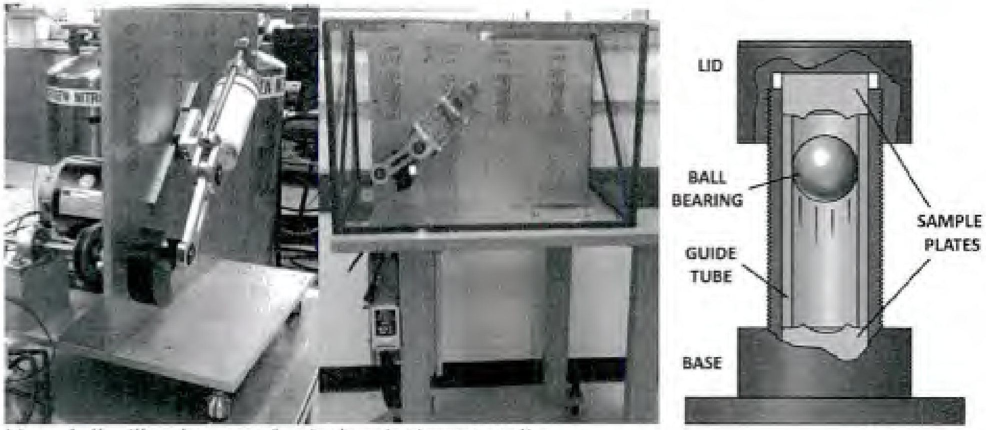

Figure 3 - Linear ball mill and concept for single-point impact studies.

1.4 Vial Sleeve Adapter

Another of the processing developments we worked together on was the creation of an adapter to allow vials from MTI Corp. to be used in cryomilling. This was not possible initially as the Teflon vial sleeves for SPEX vials are not universal. To address this, a custom sleeve with internal threading was required. This allowed the MTI Corp. vials, which are cheaper and available in a wide variety of materials, to be used in cryogenic milling for reduced contamination. Reducing weight was a central concern to alleviate stress on the SPEX arm. The stainless steel sleeve was reduced in mass to accommodate the need. Images of this apparatus are provided below.


Figure 4 - Vial Adapter for cryogenic milling with alternative milling vials.

1.5 A la carte Production Services

In addition to more elaborate design nd fabrication, we have also been able to provide quicker turn around on certain components. For instance, our production of nickel ball bearings from ECAE rods, and, more recently, the production of nickel milling vials (shown below). After my transition to a new institution, I can continue working on these items, and others.

Figure 5 - Vials produced for low-contamination milling.

2 Materials Research Outcomes

Although the development of unique equipment and processing techniques has been a central theme of our interactions, we have also productive in our work together on materials research. During the duration of this agreement (September 2015 until now) we have published six (6) articles together on nanocrystalline stabilization and oxide dispersed alloys, and we recently received a patent on the oxide reduction and expansion method. Additionally, there are two more pending articles, one in conjunction with the DREAMS lab at Virginia Tech on powder bed printing of foaming materials, and the second a combined effort of our on the production of silver foams using dual oxide mixtures. Both are being submitted to Materials and Design for publication. For convenience, I will summarize some of the key developments during our work together in the following sections.

2.1 *Development of Nanocrystalline Stability Maps*

After my tenure at your location, we further developed concepts of nanocrystalline stability related to easily identifying potential solutes for thermodynamic stabilization. This originally took the form of an Excel lookup calculator that allowed for elements to be entered and stabilization curves would be automatically plotted based on entries of temperature, solute concentration, and grain size. This was further refined in work involving the hot-stage XRD measurement of stability in Fe-Zr alloys. We then combined this experimental work with a similar stability calculation and mapping with the assistance of Mark Tschopp and other co-authors on the work. The citation information is provided below:

- Mark A. Tschopp, Efraín Hernández-Rivera, Mark A. Atwater, Kiran N. Solanki, Kris A. Darling. *A thermodynamic and kinetic-based grain growth model for nanocrystalline materials: Parameter sensitivity analysis and model extension.* Computational Materials Science. 131, pp. 250-265 (2017)

2.2 *Pore-forming Alloys and Metallic Composites*

An area that we have been working on together throughout this agreement is the development of pore-forming alloys using mechanical alloying. The process originated while I was working at your site, and since then it has been refined and further developed in a variety of ways. At the beginning of this agreement we had established some basic principles for the solid state foaming of copper powders, and we began developing strategies to control and optimize the processing. This included studying parametric effects of oxide content, foaming temperature, and foaming duration. From that we established that foaming progresses inward from the surface, and that, until foamed, the particle interior remains nanocrystalline. We next described methods for characterizing these structures, including microscopy and image analysis techniques. Because of the small pore sizes in these materials, it necessary to produce clean cross-sections for analysis, and focused ion beam sectioning has been critical to achieving that.

- Mark A. Atwater, Kris A. Darling and Mark A. Tschopp. *Solid-State Foaming by Oxide Reduction and Expansion: Tailoring the Foamed Metal Microstructure in the Cu-CuO System with Oxide Content and Annealing Conditions.* Advanced Engineering Materials; 18 (1), pp. 83-95 (2016)
- Mark A. Atwater, Kris A. Darling and Mark A. Tschopp. *Synthesis, characterization and quantitative analysis of porous metal microstructures: Application to microporous copper produced by solid state foaming.* AIMS Materials Science; 3(2), pp. 573-590 (2016)

Next, we examined ways to simplify processing and scale the process. The primary obstacle to that was the use of cryogenic milling. Although very effective at mixing and refining the microstructure, there is no current industrial-scale equivalent. Additionally, the time required to ensure the even mixing of loose metal and oxide powders may extend the processing time. Two strategies were developed to overcome these. First, low-oxygen copper was intentionally oxidized at particle surfaces. Second room temperature milling was applied. From this, it was determined that both aspects were useful in the production of foaming powder, and industrial processes were suggested to scale up from laboratory processing.

- Mark A. Atwater, Thomas L. Luckenbaugh, B. Chad Hornbuckle, Kristopher A. Darling. *Advancing commercial feasibility of intraparticle expansion for solid state metal foams by the surface oxidation and room temperature ball milling of copper.* Journal of Alloys and Compounds. 724, pp. 258-266 (2017)

Based on these efforts, we were then invited to submit a review article on metallic foams to Advanced Engineering Materials. This 33-page article included nearly 450 references covering the realm of solid state foaming. This review was well received, and it was named among the "Best of 2018" in that journal. Because of that designation, it is now an open access article, and that is expected to result in additional citing literature. That article was quickly followed by our work on porous Ni and Monel alloys using CuO or NiO separately. That work was the first departure from Cu and provided valuable insights into the use of differing oxides. The successful foaming of Ni provides new possibilities for functional applications, such as electrodes, where traditional Ni foams are often used. Other functional applications, such as the development of catalysts and heat pipe technologies, are ongoing. This is important to demonstrate the versatility of these materials, as our patent application for this process was recently granted, and we can now aggressively market the technology.

- MA Atwater, KA Darling, MA Tschopp. *Method of creating porous structures by particle expansion.* Patent No.: US 10,280,485 B2 (issued May 7, 2019).
- Mark A. Atwater, Laura N. Guevara**, Kris A. Darling, Mark A. Tschopp. *Solid State Porous Metal Production: A Review of the Capabilities, Characteristics and Challenges.* Advanced Engineering Materials; 20(7), 1700766 (pp. 1-33) (2018)
- Mark A. Atwater, Thomas L. Luckenbaugh, B. Chad Hornbuckle, Kristopher A. Darling. *Solid State Foaming of Nickel, Monel and Copper by the Reduction and Expansion of NiO and CuO Dispersions.* Advanced Engineering Materials; 20(9), 1800302 (pp. 1-10) (2018)

In the pending publications, we have extended the concepts associated with these porous structures to include additive manufacturing and multi-oxide systems. In conjunction with Virginia Tech, we have been able to take the initial steps toward creating "active" materials via 3D printing. In this case, the structures can be printed and later sintered and foamed. In other work, the use of silver as a matrix material and a combination of silver and copper oxides together. Through a combination of techniques, we have established the separate foaming steps, the microstructural evolution during multi-stage foaming, and the potential ways that this technique can be useful.

3 Final Summary

Our collaborative efforts have been both fruitful and enjoyable. We have been able to coordinate on a variety of levels and have been able to make meaningful advancements in the production and understanding of far from equilibrium materials. This area of research continues to be valuable to the scientific community and society more broadly. These efforts have contributed to the fundamental understanding of materials and are useful in numerous applications of interest to the Army. I hope we can continue to work together in the future.

Thank you for the privilege of your collaboration,

Mark Atwater, Ph.D.
Associate Professor
Department of Applied Engineering, Safety & Technology
Millersville University

Phone: 717.871.7217
Fax: 717.871.7931
Email: mark.atwater@millersville.edu

Federal Agency	US Army Contracting Command
Federal Grant Identifying #	W911NF-15-2-0105
Recipient Organization	Millersville University of Pennsylvania
Report Type	Final Report
Project Period	9/15/2015 - 4/15/2019

Federal Cash	
Cash Receipts	$112,521.96
Cash Disbursement	$113,323.97
Cash on Hand	($802.01)

Federal Expenditure and unobligated Balance	
Total Federal Funds Authorized	$117,823.36
Federal Share of expenditure	$112,521.96
Federal Share of unobligated obligations	$802.01
Total Federal Share	$113,323.97
Unobligated balance of Federal Funds	$4,499.39

Recipient Share	
Total Recipient Share required	$20,000.00
Recipient Share of expenditure	$20,000.00
Remaining recipient share to be provided	-

Please note an invoice has been submitted and approved for $802.01.
We are waiting for DFAS to transfer the funds.
Also, SF425 was sent in separate mail.