DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof. Reference herein to any social initiative (including but not limited to Diversity, Equity, and Inclusion (DEI); Community Benefits Plans (CBP); Justice 40; etc.) is made by the Author independent of any current requirement by the United States Government and does not constitute or imply endorsement, recommendation, or support by the United States Government or any agency thereof.

Final Scientific/Technical Report

Rapid Design and Manufacturing of High-Performance Materials for Turbine Blades

DE-AR-0001430

David Alman, National Energy Technology Laboratory
Michael Gao, National Energy Technology Laboratory
Michael Kirka, Oak Ridge National Laboratory
Michael Widom, Carnegie Mellon University

Award:	DE-AR-0001430
Lead Recipient:	National Energy Technology Laboratory
Project Title:	Rapid Design and Manufacturing of High-Performance Materials for Turbine Blades
Program Director:	Philseok Kim
Principal Investigator:	David Alman
Contract Administrator:	Steven Richardson
Date of Report:	April 29, 2024
Reporting Period:	[June 14, 2021 – December 31, 2023]

Table of Contents

Public Executive Summary

This research demonstrated the concept of carbide precipitation-strengthened refractory high entropy alloys (RHEA). The advantage of a precipitation strengthened alloy is all phases are in thermodynamic equilibrium promoting microstructural stability, and consequently retention of properties at elevated temperatures. Additionally, as with any precipitation strengthened – or age hardened - alloy, components can be heat-treated after manufacturing to manipulate the microstructure and optimize properties for performance. This is an advantage of the precipitation strengthened alloys over composites and ceramics materials, where the microstructure and properties are essentially fixed upon the initial materials manufacturing stage. High throughput (HT), multi-scale computer modeling was used to identifying novel RHEA compositions with desired characteristics needed for precipitation strengthening. Designs were validated by producing small ingots via are melting. The results showed that carbides precipitated and consequently, the strength of the alloys (measured in compression) increased after heat-treatment, which is the desired effect. The project also demonstrated the feasibility of producing articles from RHEA by additive manufacturing (AM). Electron beam melting (EBM) and laser direct energy deposition (L-DED) additive manufacturing methods, were explored with various processing parameters were interrogated for both methods. Sound (crack-free and dense) precipitation strengthened RHEA samples were produced via EDM AM, demonstrating the feasibility of the concept.

Acknowledgements

We would like to acknowledge ARPA-e for funding through the ULTIMATE Program through award DE-AR-0001430, with Philseok Kim, Program Manager and Pankaj Trivedi, ARPA-E Tech-SETA. The principal investigators would like to acknowledge the contributions of our colleagues who were instrumental in the execution of the research:

- Saket Thapliyal at Oak Ridge National Laboratory
- Paul Jablonski, Chantal Sudbrack, William Trehern, Saro Sarno, and Tracy Rutter at the National Energy Technology Laboratory
- Vishnu Raghuraman at Carnegie Mellon University.

Table of Figures/ Tables

Accomplishments and Objectives

The objective of this project is to demonstrate a lightweight, cost-effective, precipitation strengthened refractory high entropy alloy (RHEA) for additively manufacturing turbine blades for service at temperatures greater than 1300℃. Nickel-base superalloys have reached their temperature capability, thus there is a need for new ultra-high temperature alloys to enable increases in turbine efficiencies. The challenge lies in the needing to balance properties such as optimizing room temperature (RT) ductility, RT fracture toughness, creep resistance, density, cost, and manufacturability. Unlike conventional alloys and materials, by definition RHEA open up a huge compositional space which offers more possibilities of designing alloys for balancing properties. The goals of the project are: 1) Utilize integrated computational materials engineering (ICME) to identify a suitable RHEA composition around Nb-Mo-Ta-Ti-Zr-Hf-V-Cr-Al-C that will comprises a ductile high entropy solid solution strengthened matrix strengthened by fine precipitates of carbides; 2) Demonstrate the ICME-designed RHEA can be manufactured by directed energy deposition (DED) additive manufacturing (AM) with little to no cracking and any other undesirable microstructural features; 3) Validate the ICME and DED manufacturing approach by demonstrating the material and manufacturing process meet or exceed the phase 1 FOA targets.

A number of tasks and milestones were laid out in Attachment 3, the Technical Milestones and Deliverables, at the beginning of the project. The actual performance against the stated milestones is summarized here:

Table 1. Key Milestones and Deliverables.

Tasks	Milestones and Deliverables
Task 1: Alloy Design 1.1 Initial Alloy Design 1.2 Select alloy composition for demonstrating AM & properties. 1.3 Refine alloy compositions	**Q2: Identify at least 5 alloy compositions** that will comprise a desirable microstructure of body-centered cubic (BCC) matrix strengthened by carbide precipitates with targeted thermophysical properties (through high throughput CALPHAD calculations). Target thermophysical parameters: RT density ≤ 8.5 g/cm^3, solidus temperature ≥ 1800°C. Validate through characterization of arc melted buttons. **Actual Performance: (September 30, 2021)** High throughput CALPHAD methods were used to interrogate the Nb-Mo-Ta-Ti-Zr-Hf-V-Cr-Al-C compositional space for density, solidus temperature, carbide precipitation temperature, BCC decomposition temperature, solidification range, and cost (based on raw materials cost at the time). Over 20,000 potential compositions were identified based on the high through-put simulations. Twenty-five (25) compositions were identified for computational optimization and experimental validation (Table 2). The microstructure of all the alloys were examined in the as-cast and a heat-treated conditions and room temperature and select 1300C compression properties were examined. The results of these experiments demonstrated the feasibility of the carbide precipitation strengthened concept, as carbides formed - and the compressive strength increased- after annealing (Figure 1 and Figure 2). **Q3: Down select a couple of promising compositions and specify compositional range of alloys for powder production and AM.** Task includes computational optimization for mechanical performance and AM. Intrinsic ductility calculations will be used to identify compositional ranges that hold promise for room temperature ductility (>1.2% RT ductility and RT fracture toughness: >10 MPa/m1/2. Target for intrinsic ductility calculations: χ ≥1, B/G ≥1.75) and simulating shear instability using DFT.AM manufacturing optimization based on melt tracks experiments on arc melted buttons produced on M.2.1 to understand impacts of AM cooling conditions on microstructure and chemical segregation. Solidification range and segregation can be refined based CALPHAD calculations

Tasks	Milestones and Deliverables
	and/or identifying nucleant additions to control solidification and reduce segregation **Actual Performance: (March 31, 2022).** Based on simulations and experimental results (compressive properties and melt track experiments), RHEA 15 was selected as the alloy to demonstrate AM. Procurement of powders were initiated for AM experiments. As described in Task 2 below these powders were used to demonstrate the feasibility of the AM. **Q8: Further refine composition based on AM trials (if needed). Based on M3.3,** (eg., cracking and other microstructural defects) reassess composition per M2.2 to eliminate microstructure defects and optimize for possible electron-beam melting AM.Select additional RHEA for DED-AM and PAM based on the outcome of the assessment of RHEA-32. Complete microstructure and property assessment on RHEA 32. Complete a study of the heat-treatment of RHEA to balance ductility and strength. This includes the design and execution of experiments to optimize microstructures through post-processing (DED-AM and/or PAM) heat-treatments. **Actual Performance: (September 30, 2023).** A total of fifty-one (51) RHEA composition computational designed and properties predicted by computational means (Table 2). These included alloys that contained small additions of rare earth elements to modify grain boundaries and prevent carbide phase formation along grain boundaries. Simulations were also preformed to predict high temperature yield strength of the alloys. Small scale arc melted buttons were produced to validate several compositions and several compositions were selected for upscaling, as follows: (i) RHEA 32 powders for AM trials, and large (20 kg) plasma arc melted ingot for property (creep and fracture toughness evaluation); (ii) RHEA 37 for powder AM trials; and RHEA 51 for plasma arc melting for property evaluation.
Task 2: Additive Manufacturing (AM) 2.1 Engage Alloy Supplier 2.2 Procure Powders 2.3 AM Manufacturing	**Q1: Engage with a minimum of one industrial supplier** of refractory feedstocks to ensure manufacturability of alloy chemistry in powder form. **Actual Performance: (July 31, 2021)** Engaged a producer of refractory alloys and powders.

Tasks	Milestones and Deliverables
2.4 AM process report 2.5 Demonstrate AM manufacturing of specified alloy composition.	**Q4: Coordinate with industry or other refractory metal powder supplier to produce of powder from the composition in task 1.2 above.** Procurement contracts will consist of multiple batch of powder, with initial batch of 15 pounds minimum and baseline to ensure the target composition can be atomized and possess the necessary distribution and quality necessary for processing through DED prior to committing to a larger batch for manufacturing of test specimens. **Actual Performance: (June, 2022)** Powders were received from toll powder producer located in the United States. The powders were produced by plasma arc atomization. Because of the costs, capabilities, and scheduling, only one batch of 23 kg (50 pounds) RHEA 15 powders were procured and utilized for demonstrating the feasibility of AM. An analysis of the oxygen content of the powders were significantly higher than that of arc melted buttons or the large plasma arc melted materials (0.3 weight percent (wt%) oxygen in the RHEA powders compared to 0.06 wt% for a large plasma arc melted ingot from RHEA). The ability to find source that could provide research quantities of RHEA powders at a reasonable delivery time frame stymied research progress. **Q7: Using a design of experiments approach to optimize process parameters to fabricate density cubes to demonstrate the ability to produce samples achieving density >99.5% of theoretical with acceptable microstructure (i.e. microstructures with the target phases and no presence of undesirable defects or features).** The design of experiments for DED will focus on maximizing part density through processing, and mitigating cracking (if any) through a sampling the process parameter space of laser power, powder flow rate, and velocity. If defects such as internal microcracking or porosity is present, the plan will be to HIP the material to remove these defects. If surface breaking cracks are present in all DED sample and cannot be mitigated through DED processing science, we will then consider EBM as a back-up option for mitigating cracking through the advanced scan strategy options present in the technology and will follow a similar design of experiments approach for identifying a process space (beam current, speed) to produce crack free material.

Tasks	Milestones and Deliverables
	Actual Performance: (August, 2023) L-DED trials were conducted on the RHEA 15 powders. Three rounds of builds were made, that interrogated the following parameters: laser power, velocity, layer thickness, hatch size, scan strategy (90^o and 67^o interlayers, as well as circular strategy), stage pre-heating, and part configuration. Unfortunately, crack free material could not produce through L-DED. It was not clear if the thermal cracking was a consequence of the high oxygen content of the powder causing embrittlement or inherent to the alloy. EBM experiments were initiated that interrogated the following process parameters, beam current, speed, hatch spacing, layer thickness, beam power and substrate pre-heating. Crack free and dense material were produced through EBM. During EBM parts cool slower than L-DED, and therefore the thermal cracking is suppressed leading to crack free material. The results demonstrated the feasibility of AM for manufacturing RHEA components. **Q8: Document in a report AM process parameter** versus microstructure of selected precipitation strengthened RHEA, including lessons learned and guidelines. Document recommended AM process conditions for selected precipitation strengthened RHEA. **Actual Performance: (December 2023).** Report summarized above, in quarterly reports. **Q8: Manufacture five 5 tensile bars with <0.1mm in variation among the five tensile bars (manufactured specified to the appropriate ASTM E8/E8M standard).** Surface roughness of the samples will also be measured. **Actual Performance: (Not completed).** Due to delays in delivery of powders and demonstrating feasibility. We were not able to demonstrate consistency in manufacturing tensile bars.
Task 3: Mechanical Performance 3.1 Demonstrate mechanical performance of AM – produced RHEA	**Q8: Ensure that the RT tensile, RT fracture toughness, and creep strain of AM produced selected RHEA meet Phase 1 FOA metric. Target properties: Creep strain <2% at 200 MPa, 1300^{o}C after 100 hours; RT tensile elongation >1.5%; RT fracture toughness: >10 MPam$^{1/2}$.** One to five tests will be conducted for each property measurement.

Tasks	Milestones and Deliverables
	Actual Performance: (Not completed). As described above we were not able to produce tensile samples via AM (although we demonstrated the feasibility of AM manufacturing). Mechanical test specimen were extracted from the large Plasma Arc Melted ingot of RHEA-32 produced by a toll vender. However, the measure room temperature tensile ductility, fracture toughness, and 1300C creep properties were quite poor, as failure initiated from large casting defects in the specimens. The larger ingot of RHEA-51 was produced from a second vendor. Metallography examination of RHEA 51 indicates that this ingot appears to be more sound that the RHEA-32 ingot. This project ended prior to being able to extra tensile, however, this analysis of the properties of this alloy may be conducted under the Pennsylvania State University Phase II Ultimate project.
Task 4: Tech-2-market (T2M) plan 4.1 T2M Plan 4.2 Preliminary Techno-economic Analysis (TEA) 4.3 Final T2M Plan	**Q2 Submit initial draft of T2M** Plan highlighting potential industry partners for collaboration in development, proposed IP strategy, and tech transition goals for end of phase I. Establish plan to identify and engage technical board (to consist of a powder producer, turbine manufacturer, representatives from DoD, and university experts). Outline how this board will assist in overall technology transition strategy. **Actual Performance:** Plan submitted in September 2021. **Q4: Evaluate costs and sensitivities of down-selected alloys to validate potential to attain cost targets.** **Actual Performance: March 2023.** Cost sensitivities reported in March 2023 and June 2023 reports, based on actual costs assocaited with raw materials for RHEA 15 and RHEA 32. Conclusion that on a production case a RHEA alloy should be cost comparative to C103 Nb alloy.

Project Activities

The approach of this project was to use multi-scale computational modeling to identify promising compositions to produce a carbide precipitation strengthened RHEA to meet the performance objectives of the Ultimate project. Select promising compositions were experimentally validated through producing small 250 gram arc melted ingots for microstructural and mechanical (compression) property evaluation in the as-cast and an annealed conditions. **The results of these experiments demonstrated the feasibility of the carbide precipitation strengthened concept, as carbides formed - and the compressive strength increased- after annealing.** Based on these results, compositions were down selected for up-scaling for AM experiments and tensile, fracture toughness and creep evaluation. Twenty-three kilograms of RHEA-15 powders were procured for L-DED and EBM AM experiments. **Sound and dense articles were successfully produced via EBM-AM, demonstrating the feasibility of EBM as method to produce components from a precipitation hardened RHEA.** A large (20 kg) plasma arc melted (PAM) skull produced from RHEA-32, by a toll vendor, for extraction of samples for room temperature tensile, room temperature fracture toughness, and 1300C creep tests. Producing and testing samples from alloys produced via ingot metallurgy was a modification to the original plan, due in part to the difficulty on procuring powders. However, because initial processing does not fix the properties of precipitation strengthened alloys (unlike any composite approach to producing the alloys) ingot metallurgy approaches should be viable for the production. The measured properties were quite poor on PAM skull RHEA 32, as the failure occurred from large casting defects.

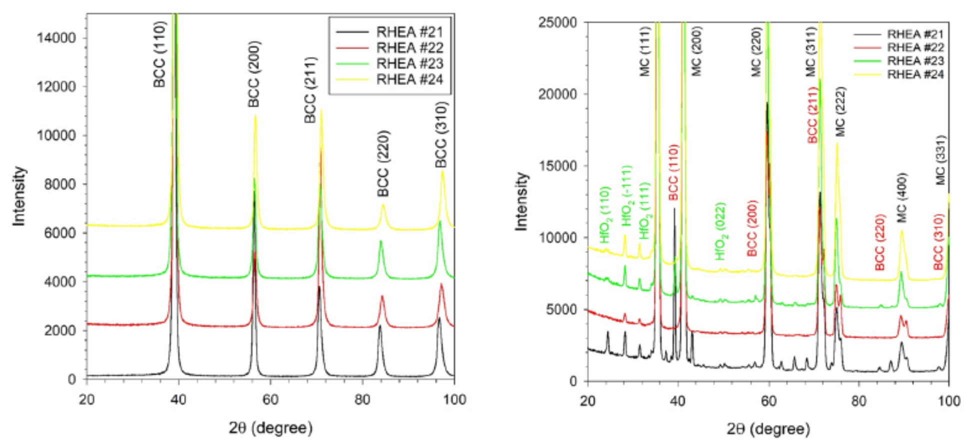

Figure 1: X-ray diffraction (XRD) results on RHEA in: (L) as-cast conditions revealing only a BCC single phase alloy and (R) the formation of MC carbides after annealing.

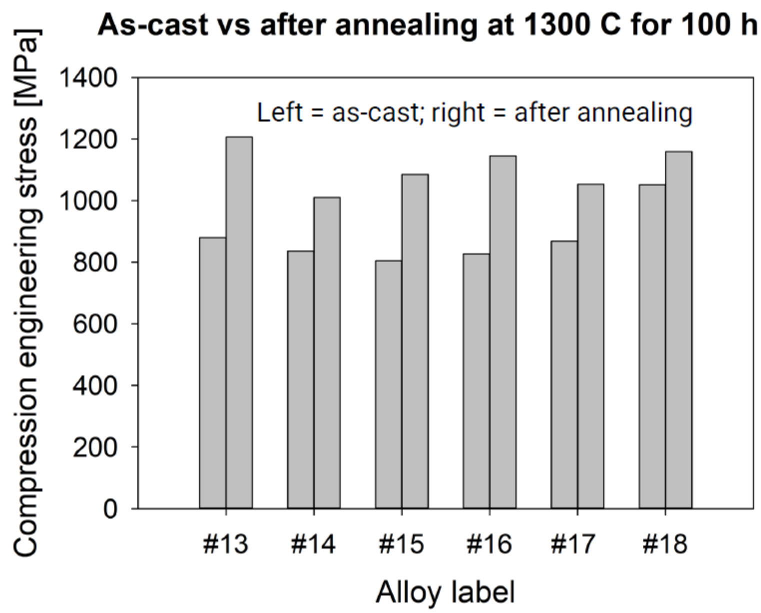

Figure 2. Comparison the room temperature yield stress in the as-cast and annealed (1300C-100hrs) for RHEA 13 through 18. The increase in yield strength after annealing is attributed to precipitation of strengthening phases.

Table 2: Calculated properties of RHEA and Measured Yield Stress in Compression

Alloy ID	Density (g/cm^3)	BCC Decom Temp (°C)	Carbide Prec T (°C)	Solidus T (°C)	Scheil T (°C)	Liquidus T (°C)	D-Para	Yield stress (RT, MPa)	YS (1300C, MPa, as-cast)
RHEA 1	8.48	616	1825	2113	1641	2325	2.83	1111	260
RHEA 2	8.48	665	1833	2094	1663	2312	2.85	1131	
RHEA 3	8.45	694	1845	2066	1687	2292	2.8	1181	
RHEA 4	8.09	880	1866	2023	1687	2257	2.79	1353	
RHEA 5	8.08	1034	1887	1983	1638	2222	2.91	1370	
RHEA 6	7.99	1173	1907	1944	1535	2185	2.82	1446	
RHEA 9	7.83	916	1362	1812	1574	2064	3.37	1348	
RHEA 10	8.12	926	1431	1853	1577	2130	3.28	784	
RHEA 13	8.59	857	1442	1962	1598	2218	3.23	833	90
RHEA 14	8.53	761	1389	2050	1618	2264	3.2	723	75
RHEA 15	8.51	733	1367	2074	1658	2269	3.21	798	
RHEA 16	8.63	700	1535	2084	1672	2282	3.22	853	
RHEA 17	8.77	721	1546	2112	1672	2309	3.14	920	150
RHEA 18	8.82	745	1504	2119	1677	2316	3.09	939	135
RHEA 19	9.21	741	1545	2159	1671	2358	2.96	1083	
RHEA 20	9.26	740	1570	2160	1664	2363	2.91	1082	210
RHEA 21	9.29	737	1594	2162	1658	2368	2.87	1199	230
RHEA 22	9.33	728	1617	2163	1654	2372	2.87	1255	226
RHEA 23	9.37	716	1640	2165	1654	2377	2.87	1263	192
RHEA 24	9.16	657	1592	2093	1538	2331	2.87	1238	
RHEA 25	8.96	743	1525	2150	1677	2341	2.87	1009	
RHEA 26	8.45	775	1520	2106	1675	2297	2.87	896	
RHEA 27	8.94	831	1789	1972	1558	2312	2.87	1299	295
RHEA 28	8.95	826	1877	1937	1558	2310	2.87	1270	110
RHEA 29	8.95	820	1930	1919	1556	2308	2.87	1293	241
RHEA 30	9.95	814	1948	1921	1556	2305	2.87	1247	190
RHEA 31	8.36	690	1831	1991	1471	2280	2.87		
RHEA 32	8.90	635	1699	2038	1502	2307	2.87		
RHEA 33	8.89	742	1756	1980	1496	2301	2.87		
RHEA 34	8.85	861	1714	1914	1429	2275			
RHEA 35	8.85	1246	1713	1803	1386	2275			
RHEA 36	8.63	847	1769	1864	1397	2257			
RHEA 37	8.66	804	1752	1153	1297	2264			
RHEA 38	9.029788	696	1730	1925	1513	2275			
RHEA 39	9.07	696	1731	1201	1484	2270			
RHEA 43	8.9	635	1687	1289	1338.3	2305	2.87		
RHEA 44	8.90	634	1684	1289	1258	2304	2.87		
RHEA 45	8.89	634	1682	1289	1145	2304	2.87	1246	
RHEA 46	8.36	696	1651	1229	978	2279	2.87	1124	
RHEA 51	11.44		2102	2489	2183	2631	2.75	694	

Project Outputs

A. Journal Articles

1. V. Raghuraman, M. Widom, S. San, M.C. Gao, Ab initio tensile tests applied to bcc refractory alloys, Physical Review Materials 7(12) (2023) 123601.

2. V. Raghuraman, M. Widom, M.C. Gao, Nonlinear deformation and elasticity of BCC refractory metals and alloys, Physical Review Materials 6(5) (2022) 053601.

B. Presentations

1. M.C. Gao, D.E. Alman, C.K. Sudbrack, P.D. Jablonski, V. Raghuraman, M. Widom, M. Kirka, "*Develop Precipitation-Strengthened Refractory High Entropy Alloys for Turbine Blades Applications above 1300 Degree Celsius*", MS&T'22, Pittsburgh, PA, October 9-13, 2022 (*invited*).
2. S. Thapliyal, J. Rojas, P. Fernandez-Zelaia, C. Ledford, A. Rossy, M. Kirka, P. Brackman, M.C. Gao, D.E. Alman, "*Direct energy deposition of Nb-containing refractory alloys: solidification behavior, microstructural evolution, and mechanical properties*", TMS 2023 Annual Meeting & Exhibition, San Diego, CA, USA, March 19-23, 2023.
3. M.C. Gao, M. Kirka, M. Widom, C. Sudbrack, V. Raghuraman, S. San, S. Thapliyal, C. Ledford, J. Rojas, B. Jordon, P. Jablonski, D.E. Alman, "*Ultimate: Affordable, Durable Precipitation Strengthened Refractory High Entropy Alloys for Use at 1300 Celsius and Above*," TMS 2023 Annual Meeting & Exhibition, San Diego, CA, USA, March 19-23, 2023.
4. M.C. Gao, D.E. Alman, S. San, W.F. Trehern, C.K. Sudbrack, P.D. Jablonski, V. Raghuraman, M. Widom, S. Thapliyal, M. Kirka, "*Rapid Design of High-Performance Refractory High Entropy Alloys Aided by Multiscale Modeling and Additive Manufacturing*," ICME 2023, Orlando, Florida, USA, May 21–25, 2023.
5. V. Raghuraman, M. Widom, M.C. Gao, "*Ab-initio tensile tests applied to BCC refractory alloys*," the 2023 International Conference on High-Entropy Materials (ICHEM 2023), Knoxville, TN, USA, June 18-22, 2023.
6. V. Raghuraman, M. Widom, M.C. Gao, "*Nonlinear deformation and elasticity of BCC refractory metals and alloys*," the 2023 International Conference on High-Entropy Materials (ICHEM 2023), Knoxville, TN, USA, June 18-22, 2023.
7. Saket Thapliyal, Julio Ortega Rojas, Brian Jordan, Michael Kirka, Sebastien Dryepondt, Christopher Ledford, Michael Gao, David Alman, *"Fusion Based Additive Manufacturing of Nb-Containing Refractory Alloys"* Powder Met 2023, Las Vegas, NV, USA, June 18-21, 2023.
8. V. Raghuraman, M. Widom, M.C. Gao, "*Ab-initio tensile tests applied to BCC refractory alloys*". 3rd World Congress on High Entropy Alloys (HEA 2023).
9. M.C. Gao, D.E. Alman, S. San, Y. Wang, W. Trehern, C.K. Sudbrack, P.D. Jablonski, V. Raghuraman, M. Widom, S. Thapliyal, M. Kirka, "*Rapid Design of High-Performance Refractory High Entropy Alloys Aided by Multiscale Modeling and Additive Manufacturing*", Materials in Nuclear Energy Systems (MiNES 2023), New Orleans, LA, USA, December 10–14, 2023.

C. Status Reports

Quarterly Status Reports entered into ARPA-e EPIC

D. Patent Applications

1. US. Patent Application: 18/426,472, Filed Jan. 30, 2024. "LOW-COST HIGH-PERFORMANCE REFRACTORY HIGH ENTROPY ALLOYS FOR GAS TURBINE BLADE APPLICATIONS ABOVE 1300 CELSIUS," Michael C. Gao, David E. Alman, Michael Kirka, Michael Widom and Saket Thapliyal.

Follow-On Funding

Additional funding committed or received from other sources (e.g. private investors, government agencies, nonprofits) after effective date of ARPA-E Award.

Project merged with Pennsylvania State University's Phase II Ultimate Award.

Table 7. Follow-On Funding Received.

Source	Funds Committed or Received
ARPA-e Ultimate	$670,000