

Center for Advanced Non-Ferrous Structural Alloys An Industry/University Cooperative Research Center

Project 56-L: Thermomechanical Processing of Refractory Multi-Principal Element Alloys for Ultrahigh Temperature Performance

Semi-annual Spring Meeting **April 2022**

- Student: Adira Balzac (Mines)
- Faculty: Dr. Amy Clarke (Mines)
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- Industrial Mentors: TBD



IOWA STATE UNIVERSITY



Project 56-L: Thermomechanical Processing of Refractory Multi-Principal Element Alloys for Ultrahigh Temperature Performance



 Student: Adira Balzac (Mines) Advisor(s): Amy Clarke (Mines) 	Project Duration PhD: September 2021 to May 2025
 <u>Problem:</u> Ni and Co alloys cannot be operated above 1200°C without coatings and cooling channels that reduce efficiency. RMPEAs can be used at higher temperatures, but thermomechanical processing is challenging. <u>Objective:</u> Design RMPEAs with higher temperature performance and develop understanding of alloy and microstructure response to thermomechanical processing above 1000°C. <u>Benefit:</u> Refractory MPEAs that can be operated above 1200°C 	 <u>Recent Progress</u> Continued coursework Gleeble thermomechanical simulator, arc melter training Initial Thermo-Calc, kinetic, and solid solution strengthening modeling for alloy down-selection Identified gaps in literature for alloy selection and modeling Submitted abstract to MS&T
will allow for significant improvements in efficiency.	 Selected material for master alloys and began making alloys

Metrics							
Description	% Complete	Status					
1. Literature review	20%	•					
2. Thermodynamic, kinetic, and solid solution strengthening modeling to select RMPEAs	50%	•					
3. High temperature thermomechanical processing of selected RMPEAs	0%	•					
4. High temperature thermomechanical processing of RMPEAs with higher oxygen and carbon levels	0%	•					
5. Characterization of RMPEAs	0%	•					

RMPEAs have potential for ultrahigh temperature applications

- Jet turbine engines
- Supersonic flight
- Nuclear reactors







Center Proprietary – Terms of CANFSA Membership Agreement Apply

Limited options for refractory properties

- Current refractory alloys have limited operability above 1200 °C
- Limits efficiency and component lifetime [4]







Limited options for refractory properties



- Current refr operability (
- Limits efficie



1 1IA 11A	Periodic Table of the Elements											18 VIIIA 8A					
H ydrogen 1.0079	2 IIA 2A											13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	2 He Helium 4.00260
Li lithium 6.941	4 Be Beryllium 9.01218											5 B Boron 10.811	6 Carbon 12.011	7 N Nitrogen 14.00674	8 O Oxygen 15.9994	9 F Fluorine 18.998403	10 Ne Neon 20.1797
Na Sodium .989768	12 Mg Magnesium 24.305	3 IIIB 3B	4 IVB 4P	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9 VIII	10	11 IB 1B	12 IIB 2B	13 Aluminum 26.981539	14 Silicon 28.0855	15 P Phosphorus 30.973762	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Argon 39.948
K tassium 19.0983	20 Ca Calcium 40.078	21 Scandiur 44.9555	Ti Titanium 47.88	23 V Vanadium 50.9415	24 2 Cr Chromium 51.9961	5 Mn anganese 54.938	26 Fe Iron 55.847	27 27 2 Co Cobalt 58.9332	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Gallium 69.732	32 Germanium 72.64	33 As Arsenic 74.92159	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Krypton 83.80
Rb ubidium 5.4678	38 Sr Strontium 87.62	39 Y Yttrik 88.90t	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 4 Mo Molybdenum 95.94	FC	44 Ru Ruthenium 101.07	45 4 Rh Rhodium 102.9055	Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn ^{Tin} 118.71	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 Iodine 126.90447	54 Xeo 131.29
CS Cesium 2.90543	56 Ba Barium 137.327	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungster 183,8	Re Rhenium 186.207	76 Os Osmium 190.23	77 7 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.9665	80 Hg Mercury 200.59	81 TI Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98037	84 Polonium [208.9824]	85 At Astatine 209.9871	86 Rn Radon 222.0176
Fr rancium 23.0197	88 Ra Radium 226.0254	89-103 F	104 Rf Rutherfordium [261]	105 Dubnium [262]	Sg Seaborgium [266]	07 Bh Bohrium [264]	108 Hs Hassium [269]	109 1 Mt Meitnerium D [268]	Ds Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Fl Flerovium [289]	115 Uup Ununpentium unknown	116 LV Livermorium [298]	117 Uus Ununseptium unknown	118 Uuuo Ununoctiur unknown
La	nthanide Series	57 Lanthanum	58 Ce Cerium	59 Praseodym	60 Nd Neodymium	61 Promethiur	62 Sm Samarium	63 Europium	64 Gadoliniur	65 Tb Terblum	66 Dysprosium	67 Ho Holmiur	68 Erbiurr	69 Tr Thullun	70 Ytterbium	71 Lu	,
A	ctinide Series	89 Actinium 227.0278	90 Th 232,0381	91 Protactinit 231.0358	92 U U um 8 238,0289	93 Neptunium 237.0482	94 Plutonium 244.0642	95 Am Americium 243,0614	96 Curium 247.0703	97 Bk Berkelium 247.0703	98 Californiur 251.0796	99 Es Einsteinin (2541	100 Fr Jum Fermiur 257.095	101 Mendelevi 258.1	102 102 Nobelium 259,1009	103 Lawrenci 12621	Im
			Alkali Metals	Alkaline Earths	Transitio Metals	n Ba Met	sic Sen tals Sen	ni-Metals I	Nonmetals	Halogens	Noble Gases	Lant	nanides /	Actinides			
	Test Temperature, °C Todd Helmenstine, sciencenotes.org																



Collaborative research





A. J. Clarke et. al. 2021.

Temperature dependence of yield stress limits thermomechanical processing window



F.G. Coury, Solid Solution Strengthening Mechanisms in High Entropy Alloys, 2018.

Predicted strength informs TMP





Difficulty in thermomechanical processing



 Presence of intermetallic phases leads to brittle failure



X-ray radiographs of selected RMPEA buttons canned in mild steel after hot rolling at 1000 °C, courtesy of ATI

A. J. Clarke et. al. 2021.

Difficulty in thermomechanical processing



 Presence of intermetallic phases leads to brittle failure





AINbTaTi

Phase stability at elevated temperatures



- Formation of deleterious phases
- Homogenization of microstructure





CrNbTaTi following heat treatment at 1400 C for 35 hours

> F.G. Coury, Solid Solution Strengthening Mechanisms in High Entropy Alloys, 2018.

Phase stability at elevated temperatures



- Formation of deleterious phases
- Homogenization of microstructure





WNbTaTi following heat treatment at 1400 C for 35 hours

F.G. Coury, Solid Solution Strengthening Mechanisms in High Entropy Alloys, 2018.

Limited predictive ability of models



- CALPHAD models limited by experimental data
- Literature focus on equimolar compositions





$Mo_{0.44}Nb_{0.3}V_{0.26}$ Nb_{0.27}V_{0.27}W_{0.46} Ta_{0.22}Ti_{0.3}W_{0.47} BCC_B2 LIQUID BCC_B2 BCC_B2 LIQUID BCC_B2#2 HCP_A3 Ta_{0.24}V_{0.33}W_{0.43} BCC_B2 1.0-BCC_B2#2 Liquid BCC BCC BCC 0.9 -0.9-BCC 0.9 Liquid Liquid 0.9-Liquid 0.8 0.8 all phases all phases all ph **b** 0.6 5 Nolume fracti Volume fractio 0.3-HCP 0.3 0.2 -0.2 0.2 0.2 **BCC #2** 0.1-**BCC #2** 0.1 0.1 -0.1 0.0-2500 0.0-500 2000 3000 0.0 0.0 500 1000 2500 300 Temperature [°C] 2500 3000 500 1000 1500 2000 500 1000 1500 2000 2500 3000 Temperature [°C] A Temperature [°C] Temperature [°C] **MoNbV** NbVW TaTiW TaVW BCC_B2 BCC_B2 LIQUID BCC_B2 BCC_B2 BCC_B2#2 LIQUID 1.0 -1.0 1.0 -LIQUID 1.0 BCC_B2#2 Liquid **BCC #2** HCP_A3 Liquid BCC Liquid 0.9-BCC 0.9-0.9-0.9-BCC Liquid 0.8-0.8 0.8 0.8 all phases of all phases 0.7 all phas alle **6** 0.6 **b** 0.6 of Volume fraction fraction 6 0.5 **e** 0.4 0.4 -0.4 **HCP** 0.3 0.3-0.3-0.3 BCC 0.2 0.2 0.2-0.2-**BCC #2** 0.1 0.1 0.1 0.1 -0.0-0.0-0.0-0.0 500 1500 2000 2500 3000 500 1000 1500 2000 2500 3000 500 1000 1500 2000 2500 300 1000 1500 2000 2500 3000 500 A Temperature [°C] \mathbb{A} Temperature [°C] Temperature [°C] Temperature [°C]

Initial ternary alloy selection

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TMP to control microstructures

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- Recrystallization
 - Heterogeneous necklace structure





Eleti et. al. Acta Materialia (2020).

TMP to control microstructures

CANFSA CENTER FOR ADVANCED NON-FERROUS STRUCTURAL ALLOYS

- Dynamic recrystallization
 - Heterogeneous necklace structure
 - Cryo-rolling and annealing









EBSD of HfNbTaTiZr (a) cryo-rolled to 90% reduction and annealed at (b) 800 °C, (c) 1000 °C, (d) 1250 °C, (3) 1400 °C for 1 hour

Veeresham, International Journal of Materials and Metallurgical Engineering (2021).

THE AVERAGE GRAIN SIZE OF TAHFNBZRTI CRYO ROLLED AND ANNEALED
TEMPERATURES

	CRYO-90%	800°C	1000°C	1250°C	1400°C
Average Grainsize(µm)	0.22	1.27	29.21	22.12	51.37
Standard Deviation	0.12	1.97	18.60	15.02	41.58

Effects of interstitials on conventional refractory alloys





Effect of carbon on as-cast hardness of Ta-W-Hf





R.W. Buckman, Jr., R.R. Begley, NASA, Report No. NASA SP-245, 1970, pp. 19-37 R.W. Buckman, Jr., JOM, 2000, 53:40-41

Exploring the role of oxygen and carbon on RMPEAs



Fe, Ni, Co

ac Interstitial C, O 4000 C + Mo = MoC IONIC LIQ 2 + 2W = W -20 3750 3000 -40 3500 -60 C + Si = SiC 3250 IONIC_LIQ BCC_A2 -80 3000 2500 -100 2750 -120 BCC_A2 HCP A3 105 **2** 2500 KJ/m -140 2250 2250 2000 2000 2000 ['] ΰ per gfw FC Temperature Gibbs Energy 10 BCC A2+NBO1 -200 NB01+NB02 BCC A2+HCP A3 FCC A1+HCP A3 C + 2Ta = Ta₂C 1500 1750 -220 1500 -240 -260 1250 1000 -280 1000 -300 750 10-2 -320 500 500 5 10 20 0 15 -340 2 3 5 7 8 0 1 4 6 9 Mass percent O 200 400 0 600 800 1000 1200 1400 1600 1800 2000 2200 2400 2600 2800 3000 3200 Mass percent C Т, К

Courtesy Noah Philips, ATI

Interstitial effects



• NbTaW_{0.5}(Mo₂C)_x (x=0-0.25)



Compressive stress-strain curves at (a) 1200 C and (b) 1400 C

Wu et. al., Journal of Alloys and Compounds (2022).

Interstitial effects

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- NbTaW_{0.5}(Mo₂C)_x
- Nitrogen doped NbTaTiZr



Effect of nitrogen content on average as-cast grain size



Wang et. al. Materials and Design (2022).

Next steps



- Equilibrium phase data
 - Identify off-equimolar compositions of interest
 - Develop heat treatment to reach equilibrium state
 - Characterization of equilibrium structure
 - NbTaTi, NbTiZr, MoNbV, NbVW, TaTiW, TaVW
- Identify quaternary compositions of interest
 - TC-EARS and CALPHAD modeling
- Initial characterization and thermomechanical processing
 - Arc melting to produce buttons
 - Gleeble thermomechanical simulations
 - SEM, TEM, XRD

Gantt Chart





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Challenges & Opportunities



- Making material
 - Melting compositions containing W difficult due to high melting temperature
- Studying equilibrium structures
 - Long times and high temperatures needed
 - Stability of as-cast microstructure
- Thermomechanical processing
 - Gleeble
- Characterization
 - SEM, TEM, and XRD

Thank you! Adira Balzac abalzac@mines.edu

References



A. J. Clarke, Technical proposal: Thermomechanical processing of refractory multi-principal element alloys for ultrahigh temperature performance.
 O.N. Senkov, D.B. Miracle, K.J. Chaput, J.P. Couzinie, Development and exploration of refractory high entropy alloys - A review, Journal of Materials Research.
 (2018) 3092–3128. https://doi.org/10.1557/jmr.2018.153.

[3] D. B. Miracle, O. N. Senkov, A critical review of high entropy alloys and related concepts, Acta Materialia 122 (2017), 448–511.

[4] C.C. Juan, M.H. Tsai, C.W. Tsai, C.M. Lin, W.R. Wang, C.C. Yang, S.K. Chen, S.J. Lin, J.W. Yeh, Enhanced mechanical properties of HfMoTaTiZr and

HfMoNbTaTiZr refractory high-entropy alloys, Intermetallics. 62 (2015) 76–83. https://doi.org/10.1016/j.intermet.2015.03.013.

[5] O.N. Senkov, S. Gorsse, D.B. Miracle, High temperature strength of refractory complex concentrated alloys, Acta Materialia. 175 (2019) 394–405.
 [6] F.G. Coury, Solid Solution Strengthening Mechanisms in High Entropy Alloys, 2018.

[7] C.C. Wojcik, Thermomechanical processing and properties of niobium alloys, in: International Symposium Niobium, 2001: pp. 163–173.

[8] R.W. Buckman Jr., R.C. Goodspeed, Precipitation strengthened tantalum base alloy, ASTAR-811C, 1971.

[9] P. P. Cao, H. L. Huang, S. H. Jiang, X. J. Liu, H. Wang, Y. Wu, Z. P. Lu, Microstructural stability and aging behavior of refractory high entropy alloys at intermediate temperatures. Journal of Materials Science & Technology (2022), 122, 243–254. <u>https://doi.org/10.1016/j.jmst.2021.12.057</u>

[10] R. Wang, Y. Tang, Z. Lei, Y. Ai, Z. Tong, S. Li, Y. Ye, S. Bai, Achieving high strength and ductility in nitrogen-doped refractory high-entropy alloys, Materials and Design (2022), 213. https://doi.org/10.1016/j.matdes.2021.110356

[11] S. Wu, D. Qiao, H. Zhao, J. Wang, Y. Lu, A novel NbTaW0.5 (Mo2C)x refractory high-entropy alloy with excellent mechanical properties. Journal of Alloys and Compounds (2022), 889. https://doi.org/10.1016/j.jallcom.2021.161800

[12] R. R. Eleti, A. H. Chokshi, A. Shibata, N. Tsuji, Unique high-temperature deformation dominated by grain boundary sliding in heterogeneous necklace structure formed by dynamic recrystallization in HfNbTaTiZr BCC refractory high entropy alloy. Acta Materialia (2020), 183, 64–77.

[13] M. Veeresham, Microstructure and texture evolution of cryo-rolled and annealed ductile TaNbHfZrTi refractory high entropy alloy. International Journal of Materials and Metallurgical Engineering (2021), 15(11).

[14] R.W. Buckman, Jr., R.R. Begley, NASA, Report No. NASA SP-245, 1970, pp. 19-37

[15] R.W. Buckman, Jr., JOM, 2000, 53:40-41