An Integrated Study on a Novel High Temperature High Entropy Alloy

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Introduction

- Project Period: 10/1/2013 --- 9/30/2015
- Project Manager: Jessica Mullen and Steven Markovich
- Project Objectives:

(1). Perform molecular dynamics (MD)/Monte Carlo (MC) and interface energy HPC simulation on the HEA models to screen out the potential high temperature and high pressure oxidation resistant and low temperature ductile ODS HEA candidates.

(2). Perform experiments on the high temperature and high pressure property of the most promising ODS HEA systems from the simulation.

(3). Train students and postdocs on HEA modeling, HPC simulation, sample synthesis and characterization, and texture related dislocation analysis techniques.

Introduction

1. The high temperature high entropy alloys (HEAs), such as NbMoTaW and TaNbHfZrTi, show considerable promise to have higher operating temperature, good mechanical properties at high temperature, major improvement in high temperature oxidation resistance and structure stability.

2. The recent development of molybdenum (Mo) alloys, with nano-scale powders of transition metal oxides (La_2O_3) that sparsely dispersed in the Mo matrix named oxide dispersion strengthened (ODS) alloy, giving over 800 MPa yield strength and ~40% room temperature tensile elongation, is based on the idea that impurities within the crystal can act as pinning centers for dislocations.

3. To save time and expense, we need integrate computation with experiment to avoid triae.

Methods We Used

1. Perform *ab initio* density functional theory (DFT) method based molecular dynamics (MD) and long time Monte Carlo HPC simulations on the high temperature and high pressure behavior of the potential candidate ODS HEAs. The interface energies and bonding of different dopant elements and concentrations will be compared and optimized to obtain the most stable structure.

2. Experimentally validate the predicted potential high performance high temperature HEAs. High temperature oxidation, corrosion, and microscopy tests will be performed at locally. Special in-situ high pressure tests on the new materials will be performed at Lawrence Berkeley National Laboratory (LBNL) Beamline 12.2.2.

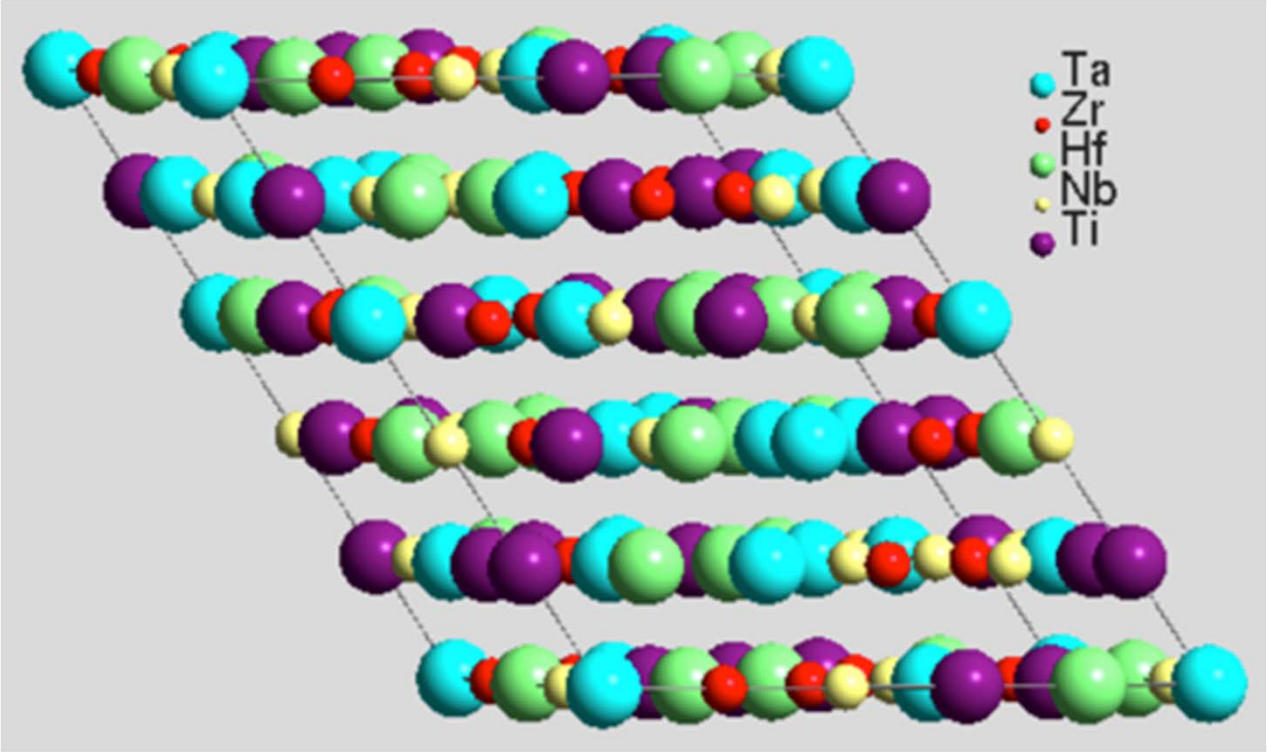
Current Status and Results

1. We had performed simulation on HEAs: AlxFeCoCrNi, NbHfZrMoTaTi, and MoNbTaTiVW.
2. We had performed synchrotron XRD compress and decompress experiment on the AlxFeCoCrNi, NbHfZrMoTaTi, MoNbTaTiVW.
3. We trained postdoc and students on the computational material design, HPC simulation, materials synthesis, and characterization using synchrotron XRD under high pressure shear stress.

Simulation Results: HfNbTaTiZr

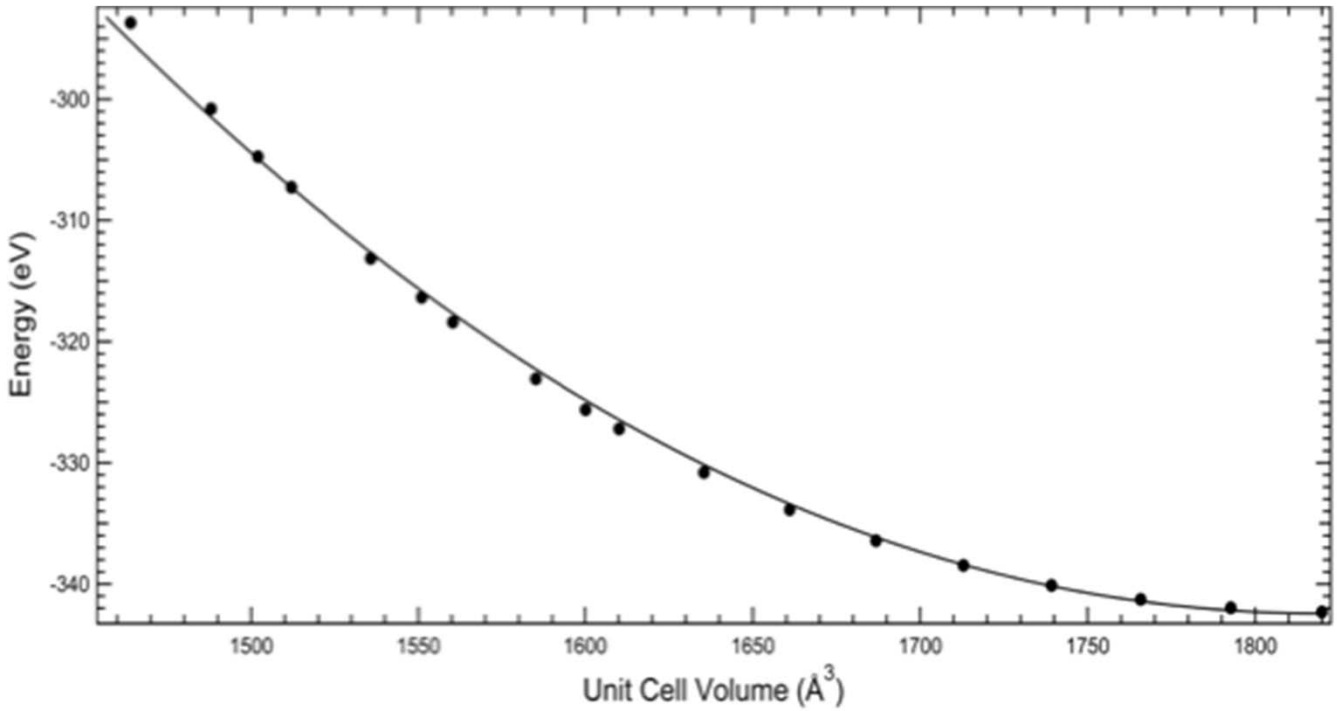
We have been using VASP codes (MedeA package) to efficiently optimize and predict possible stable HEA structures. In our VASP simulation, we performed the *ab initio* density functional theory (DFT) based electronic structure simulations and optimized the AlFeCoCrNi, crystal structure. The local density approximation (LDA) PAW potentials were used with 400 eV plane wave energy cutoff. The energy convergence was set to be less than 0.01 meV while the force convergence was set at less than 0.2 meV/Å.

Simulation Results: HfNbTaTiZr



The model will be used in simulation for NbHfZrTaTi.

Simulation Results



The black dot - compression data.
The best fit solid line of the Birch–Murnaghan equation.
The bulk modulus 198 Gpa.

Oxidation Simulation Results

- The nudged elastic band (NEB) method in VASP is used to investigate the alloy's oxygen diffusion barrier.
- The average diffusion barrier is at ~ 0.2 ~0.5 eV higher than those of pure Nb, which is ~1.2 eV.

Synchrotron XRD Results: HfNbTaTiZr and MoNbTaTiVW

Our preliminary compress and decompress XRD data shows that the crystal structure is very stable up to ~ 25 GPa and decompress to ambient pressure. The high temperature and pressure HfNbTaTiZr data and texture of MoNbTaTiVW data are processing.

$Al_xFeCoCrNi$ Hot Corrosion

1. Different compositions of Al HEA samples $Al_xFeCoCrNi$ in the presence of molten mixture of $Na_2SO_4+V_2O_5$ (50% : 50%) at 900 ^oC were tested.

2. Hot corrosion in 2 cycles 8 hours.

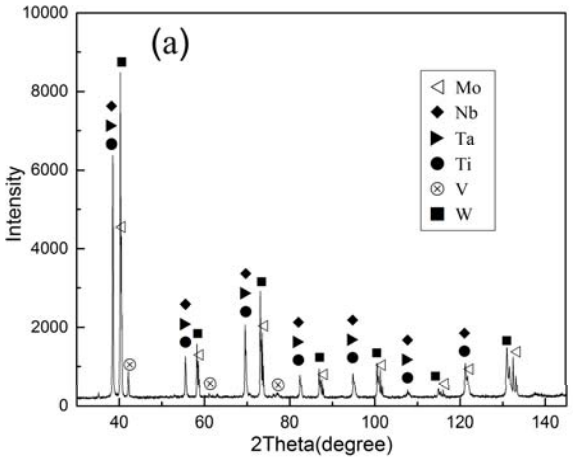
Results:

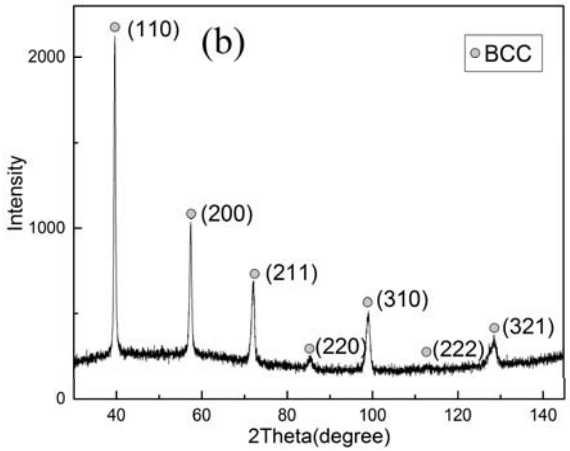
1. $Al_{0.3}FeCoCrNi$ hot corrosion has the thinnest corrosion layer;
2. $Al_{2.0}FeCoCrNi$ hot corrosion has the thickest corrosion layer;
3. $Al_{1.0}FeCoCrNi$ has better room temperature ductility.

Senary Refractory High-Entropy Alloy MoNbTaTiVW

- The design approach: CALPHAD predict single phase BCC MoNbTaTiVW (NETL).
- XRD & SEM (LSU).
- The observed elemental segregation agrees well with the solidification prediction using the Scheil model.
- The lattice constant, density, and micro-hardness were measured to be 0.3216 nm, 4.954 GPa, and 11.70 g/cm^3 respectively.
- The atomic size difference, the Ω parameter, enthalpy of mixing, and entropy of mixing for MoNbTaTiVW HEA are 3.1%, 11.1, -3.4 kJ/mol, and +13.39 J / K-mol respectively.

Senary Refractory High-Entropy Alloy MoNbTaTiVW





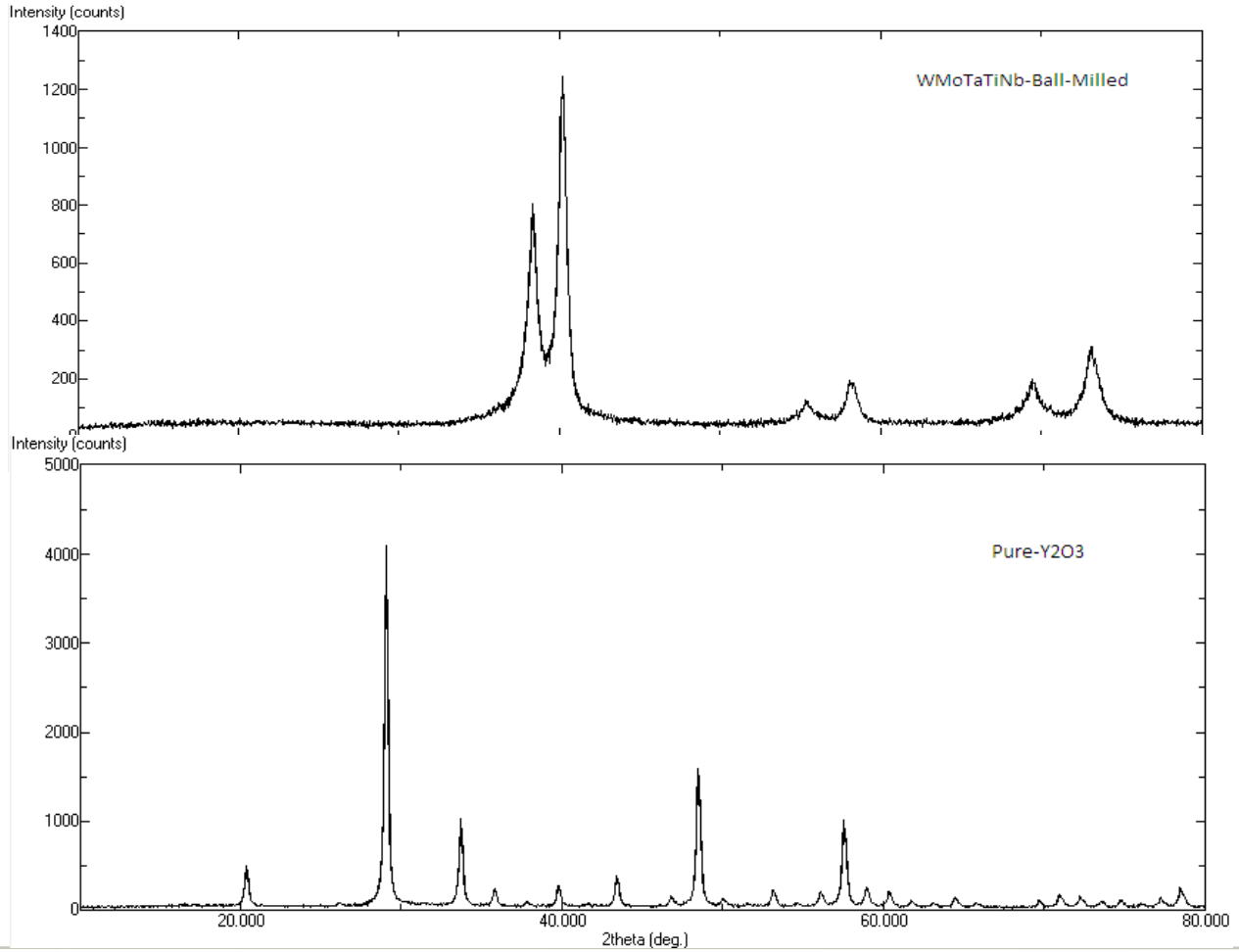
XRD patterns of MoNbTaTiVW in the (a) pre-melting powder mixture and (b) as-solidified state

Senary Refractory High-Entropy Alloy MoNbTaTiVW

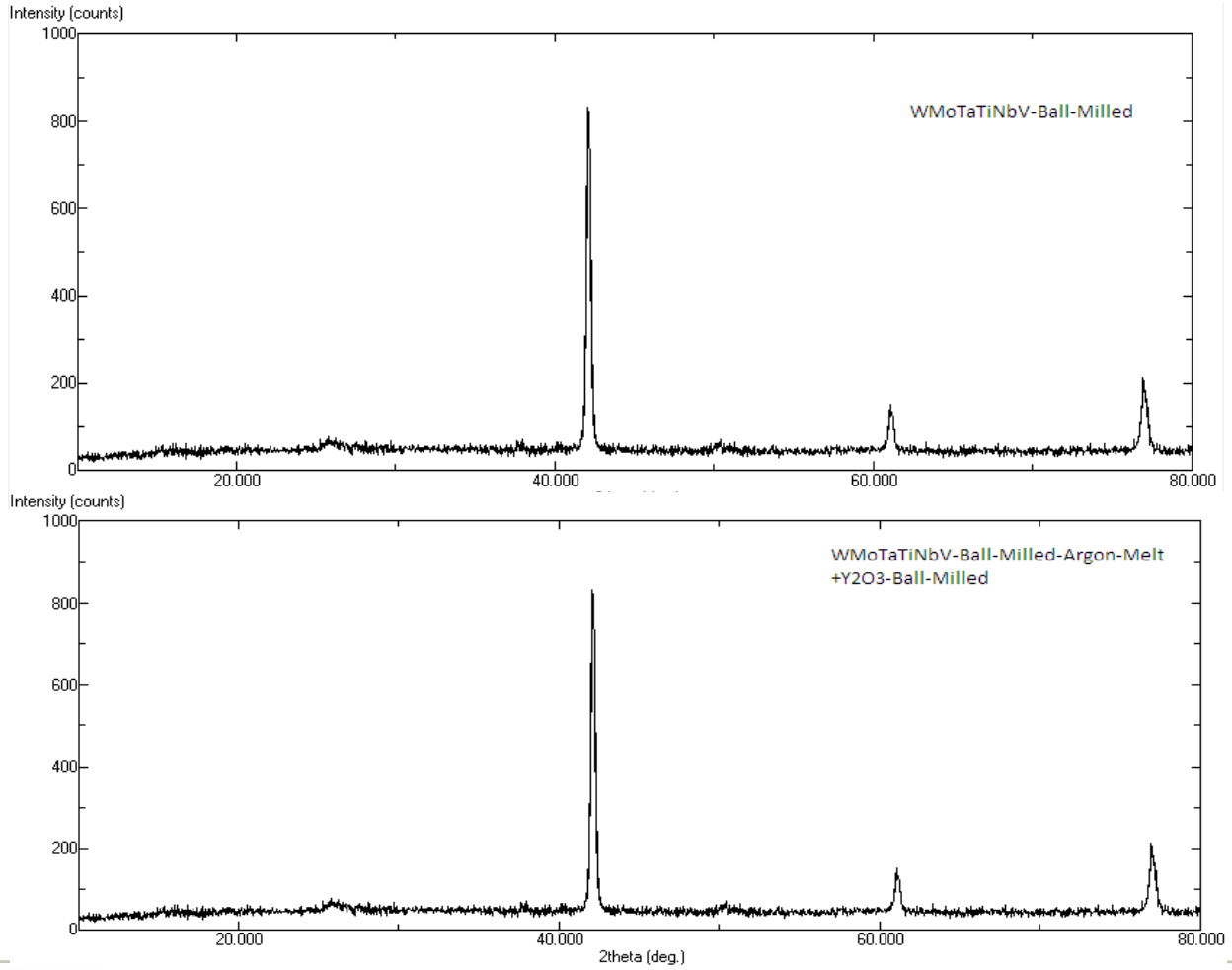
The lattice constant a, Vickers hardness H_v, density ρ, the melting temperature T_m, atomic radius r, and the Pauling Electronegativity of the HEA alloy and the pure metal feedstock.

Metal	Mo	Nb	Ta	Ti	V	W	Alloy Est.	Alloy Exp
a, nm	0.3147	0.3301	0.3303	0.2950	0.3039	0.3158	0.3174	0.3216
H_v, MPa	1530	1320	873	970	628	3430	1488	4954
ρ, g/cm^3	10.28	8.57	16.65	4.51	6.11	19.25	11.19*	11.70
T_m, ^{o}C	2623	2477	3017	1668	1910	3422	2553.35	-
r, Å	1.40	1.47	1.47	1.46	1.35	1.41	1.43	-
Pauling Electronegativity	2.16	1.6	1.5	1.54	1.63	2.36	1.80	-

ODS MoNbTaTiVW



ODS MoNbTaTiVW



Publication and Awards

1. Paper published:

- "Senary refractory high entry alloy MoNbTaTiVW", B. Zhang, M. Gao, Y. Zhang, S. Yang, and S. Guo, Materials Science and Technology, 2015, in printing.
- "Detecting grain rotation at the nanoscale", B. Chen, K. Lutker, J. Lei, J. Yan, S. Yang, and H.K. Mao, PNAS **111**, 3350 (2014).

2. Conference presentations:

- "First principles simulation on pressure induced ductility change in sulfur doped nickel", Cheng Guo, Shizhong Yang, Bin Chen, and Jinyuan Yan, LASiGMA Annual Meeting, Baton Rouge, Louisiana, April 20, 2015.
- "Electronic structures of HfMoNbTaTiZr alloy", S. Yang, L. Tan, C. Guo, E. Khosravi, and D. Bagayoko, APS March Meeting, Denver Colorado, March 5, 2014.

Awards

3. Awards:

- LINK award, NSF/LA-BOR, with $6,000, 4/18/2014 – 4/17/2015.
- RAP Award, “Materials Design and Process Optimization for Selective Laser Melting Based Advanced Manufacturing”, LASPACE, $89,851, 12/1/2014 – 10/31/2015 (PI: Guo, Co-PI: Yang).

Future Work

1. Continue to screen the interface models and perform *ab initio* HPC simulation to study the high temperature corrosion and low temperature ductility. The elastic constants and diffusion property will also be simulated. (Part of the mechanical property simulation will be in collaborating with UTK and UIUC).

2. Experimentally validate the predicted ODS HEAs: synthesize samples and characterize the high temperature and low temperature properties.

3. Students and postdocs training on ODS HEA simulation and experiment validation.

Acknowledgement

- NETL: Jessica Mullen, Steven Markovich, and Harolynne Blackwell.
- Graduate students: Boliang Zhang, Zhi Tang, Jialin Lei, Cheng Guo, and Daniel Hart; undergraduate students: Michael Jackson, Megan Jones, and Yalin Liu.
- Postdocs: Drs. Liuxi Tan, Oleg Starovoytov.
- Drs. S. Guo, P. Liew, E. Khosravi, J. Yan, and B. Chen.
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