# An Integrated Study on a Novel High Temperature High Entropy Alloy

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**Southern University and A & M College**

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# Outline

Introduction
Methods
HEA Alloy Simulation and Experiment
Future Work
Acknowledgement

# Introduction

- Project Period: 10/1/2013 --- 6/30/2016
- Project Manager: Jessica Mullen and Steven Markovich
- Project Objectives:

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

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

(3). Train students and postdocs.

# Introduction

1. The high temperature high entropy alloys (HEAs), such as HfNbTaTiZr, 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 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

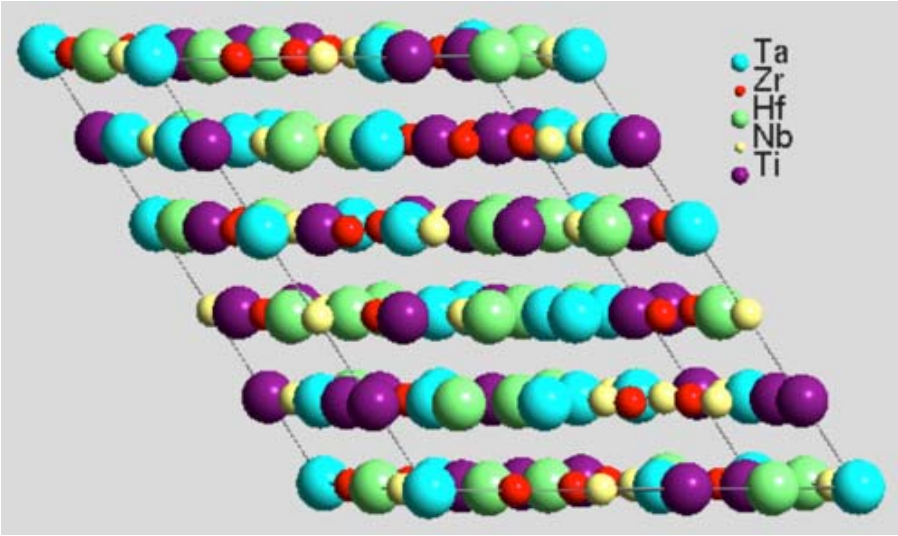
1. Perform *ab initio* density functional theory (DFT) method based molecular dynamics (MD) and long time Monte Carlo HPC simulations on the high temperature and high pressure behavior of the potential candidate HEAs. The interface and bonding of different dopant elements and concentrations will be compared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

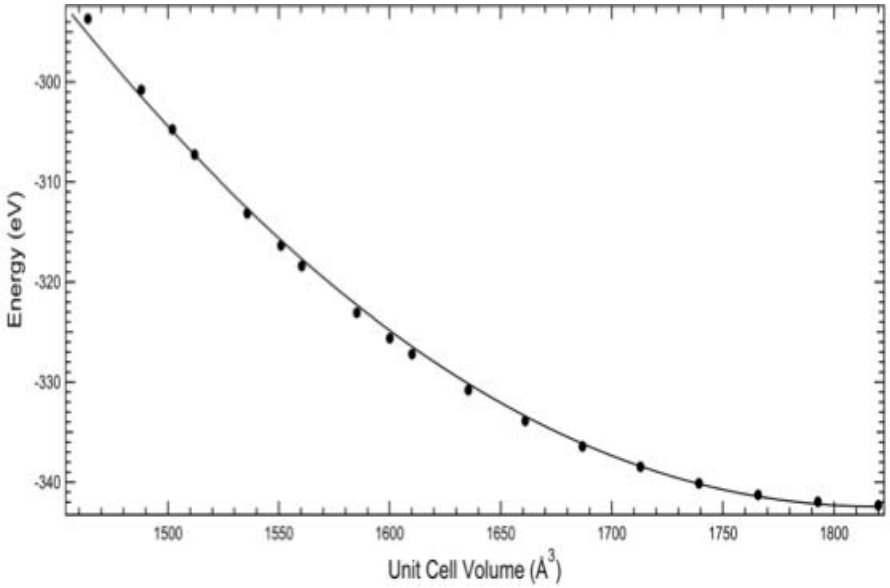
2. Experimentally validate the predicted potential high performance high temperature HEAs. High temperature oxidation, corrosion, and microscopy tests will be performed locally. Special in-situ high pressure tests on the new materials will be performed.

# Current Status and Results

1. We had performed simulation on HEAs and HEA/oxide: AlxFeCoCrNi, HfMoNbTaTiZr, MoNbTaVW, HfNbTaTiVZr, and MoNbTaTiVW, and MoNbTaVW/$Y_2O_3$.
2. We had performed synchrotron XRD compress and decompress experiment on the AlxFeCoCrNi, HfMoNbTaTiZr, MoNbTaTiVW.
3. We trained postdoc and students on the computational material design, HPC simulation, materials synthesis, and characterization using regular XRD, SEM, DSC, and synchrotron XRD under high pressure shear stress.

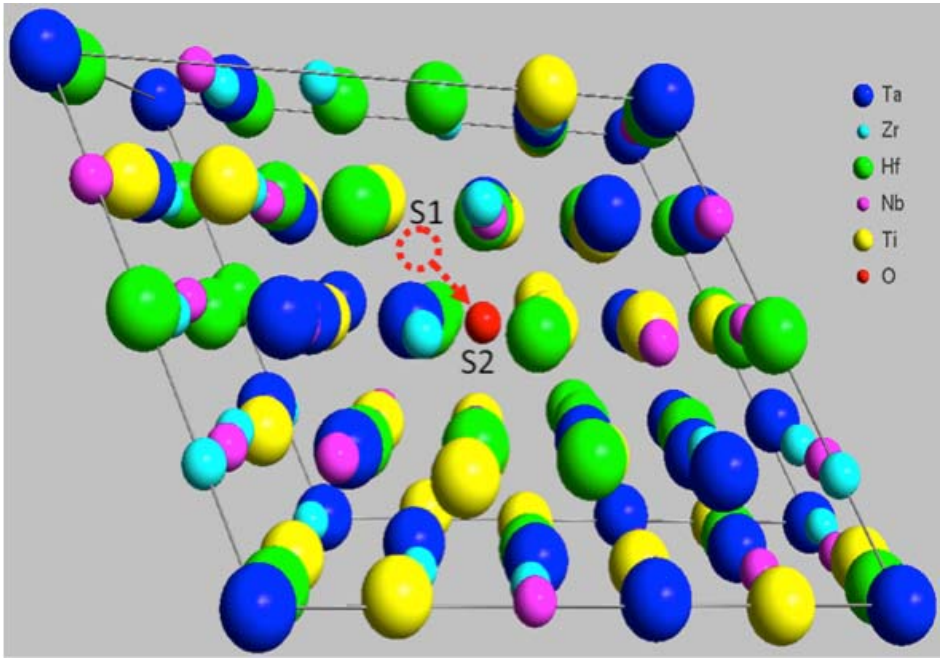
# Simulation Results: HfNbTaTiZr




**Left: The model will be used in simulation for HfNbTaTiZr. Right: The best fit solid line of the Birch–Murnaghan equation. The bulk modulus 198 GPa.**

# Oxygen Diffusion Simulation: HfNbTaTiZr

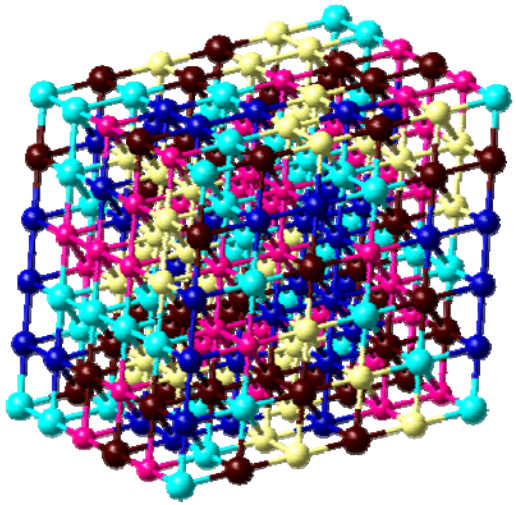



Model of HEA HfNbTaTiZr for oxygen diffusion calculation.

# 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.

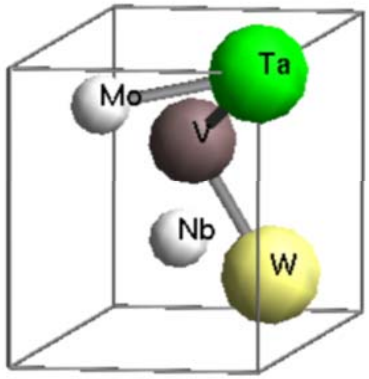
# Large HEA Special Quarsirandom Structure

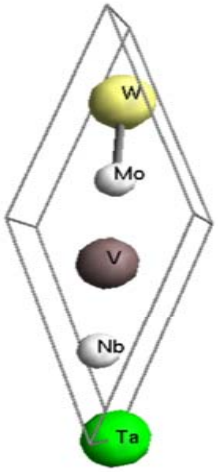


**The 125 atom ball & stick special quarsirandom structure model of MoNbTaVW. Dark blue balls are standing for Mo atoms, yellow for Nb, light blue for Ta, red for V, and brown for W. The initial lattice parameters are: a = b = c = 11.2543 Å, and α = β = γ = 109.47°.**

**The elastic constant values calculated are higher using GGA with experiment lattice constants. Full lattice and atomic relaxation is necessary to reach consistent results compared with our earlier simulation results.**

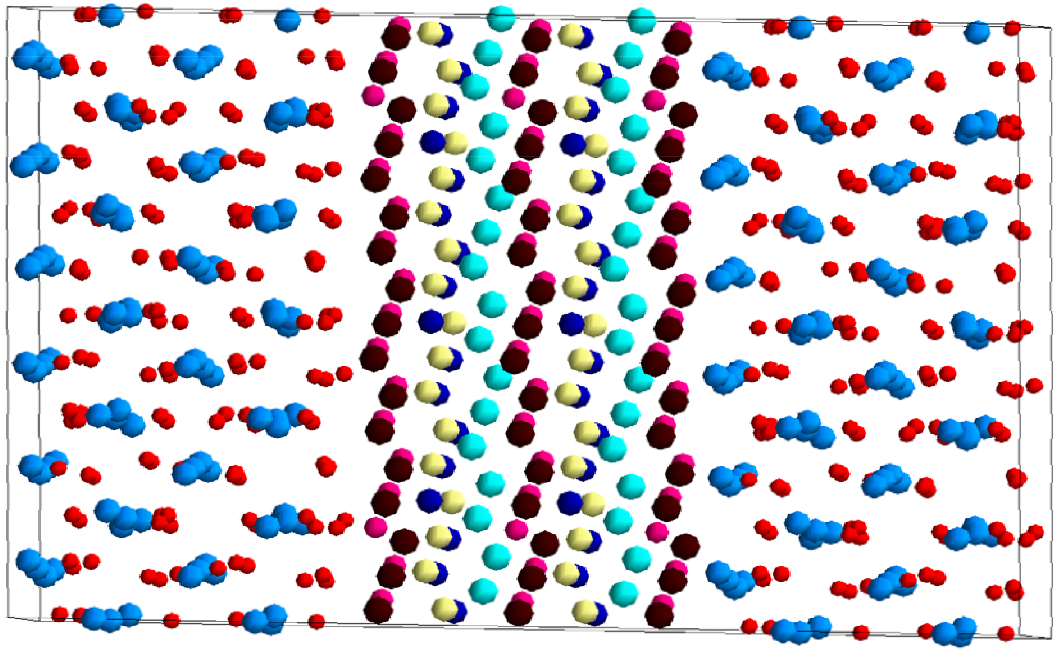
# Small Set of Ordered Structures MoNbTaVW


Three ordered MoNbTaVW structures were built and optimized for efficient mechanical, electronic structure, and thermal dynamics (high T) properties screening and prediction.

# Interface Model



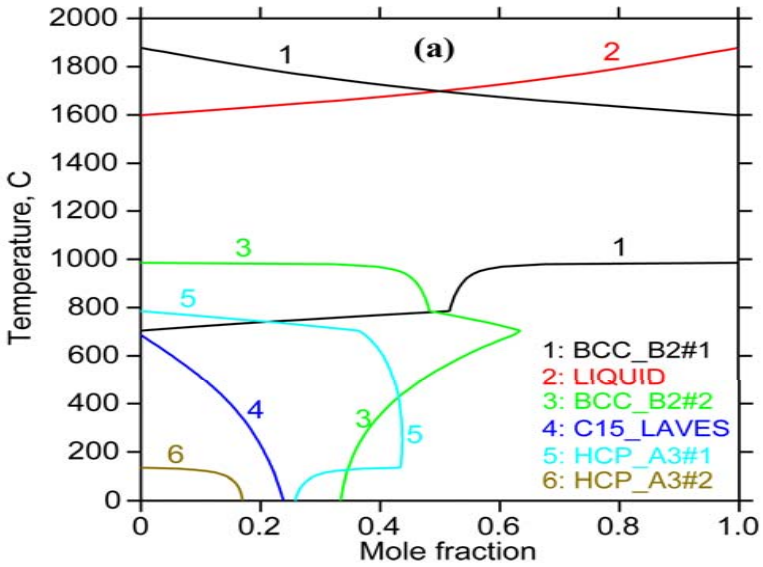
MoNbTaVW/$Y_2O_3$ interface model: the sky blue ball stands for Y atom, red for O, light blue for Ta, yellow for Nb, pink for V, dark blue for Mo, and black for W. There are 192 Y atoms, 288 O atoms, 34 Ta/Nb/Mo, and 51 V/W with total 694 atoms are included in our tentative running interface model.

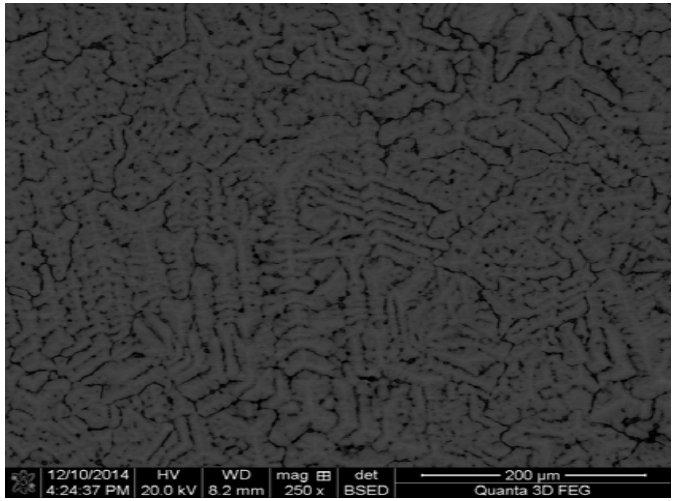
This model is perfect for studying interface properties but the computer CPU time expense is very high. An alternative interface with ~ 350 atoms was built and under testing.

# Senary Refractory High Entropy Alloy HfNbTaTiVZr

- The design approach: CALPHAD predict single phase BCC HfNbTaTiVZr (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 0.32 nm, 9.36 g/cm$^3$, and 5.48 GPa, respectively.
- The atomic size difference, the Ω parameter, enthalpy of mixing, and entropy of mixing for HfNbTaTiVZr HEA are 5.6%, 5.09 kJ/mol, and +14.59 J/K/mol respectively.

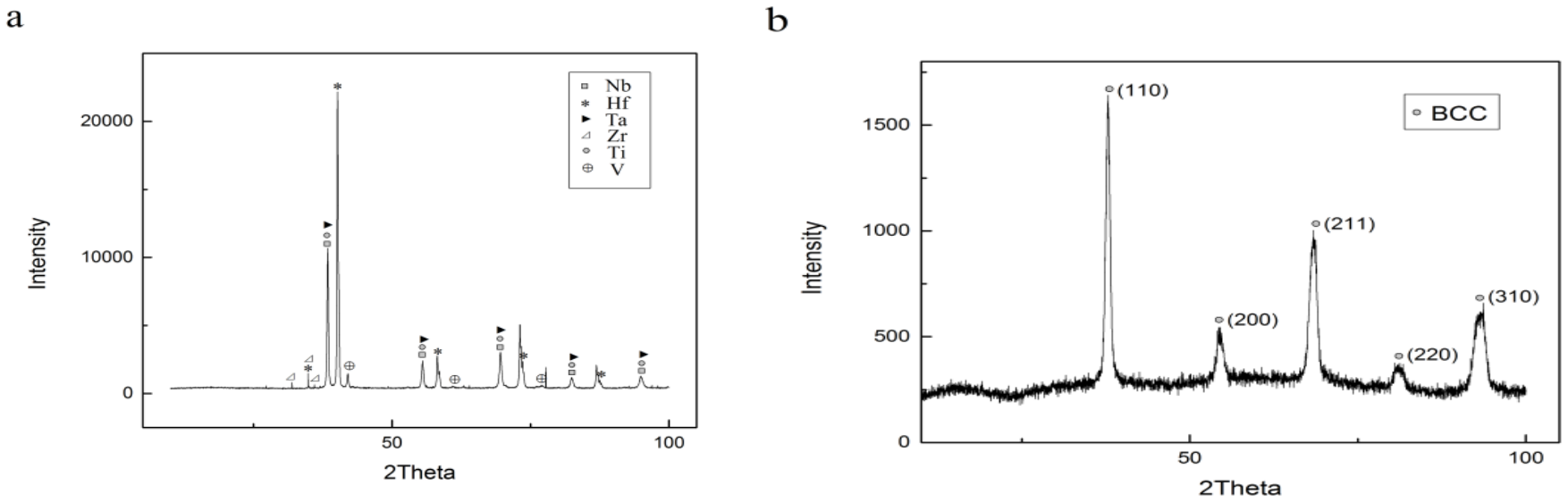
# Senary Refractory High-Entropy Alloy HfNbTaTiVZr



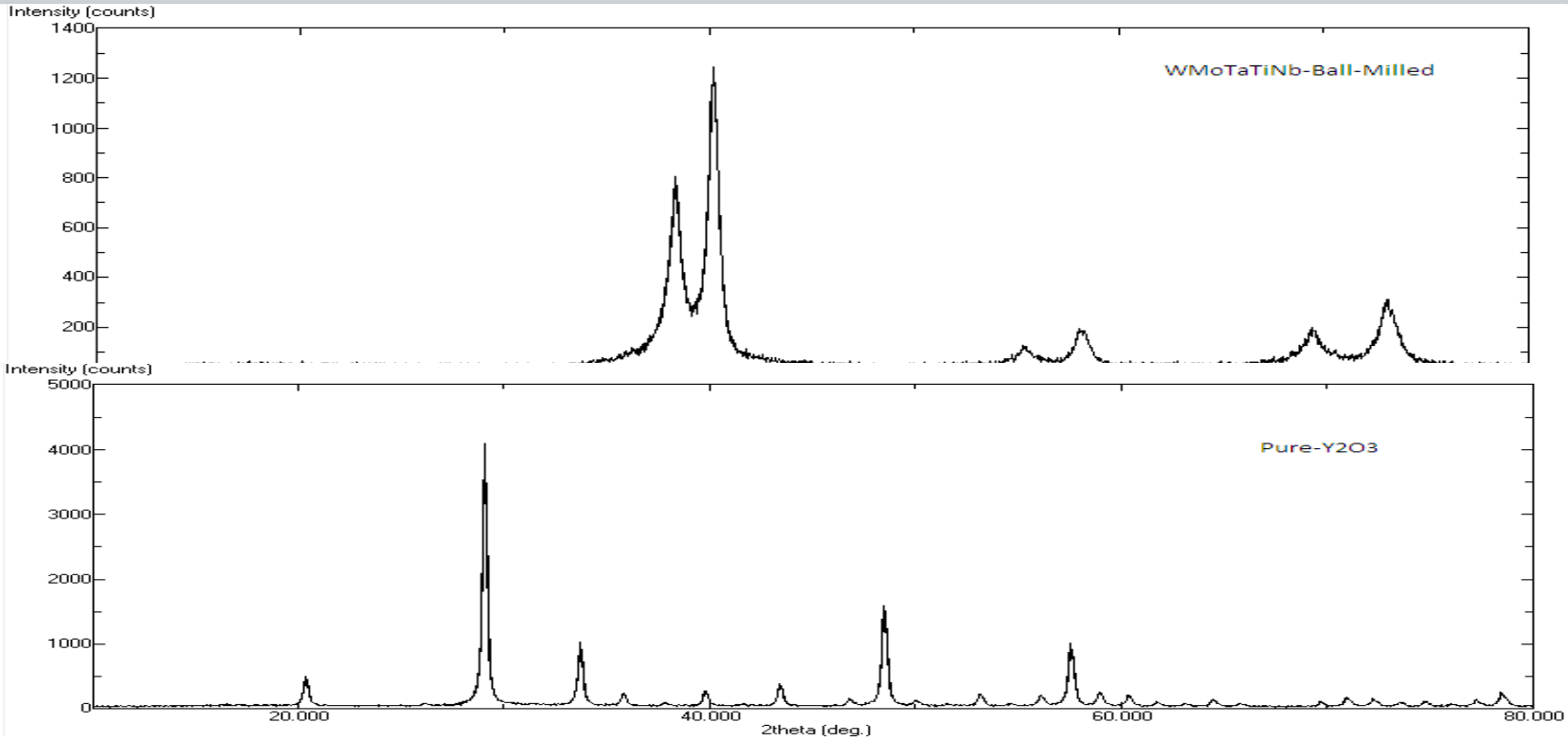

Phase Diagram(left and SEM backscatter electron images of an etched cross-section of HfNbTaTiVZr alloy

# Senary Refractory High Entropy Alloy HfNbTaTiVZr

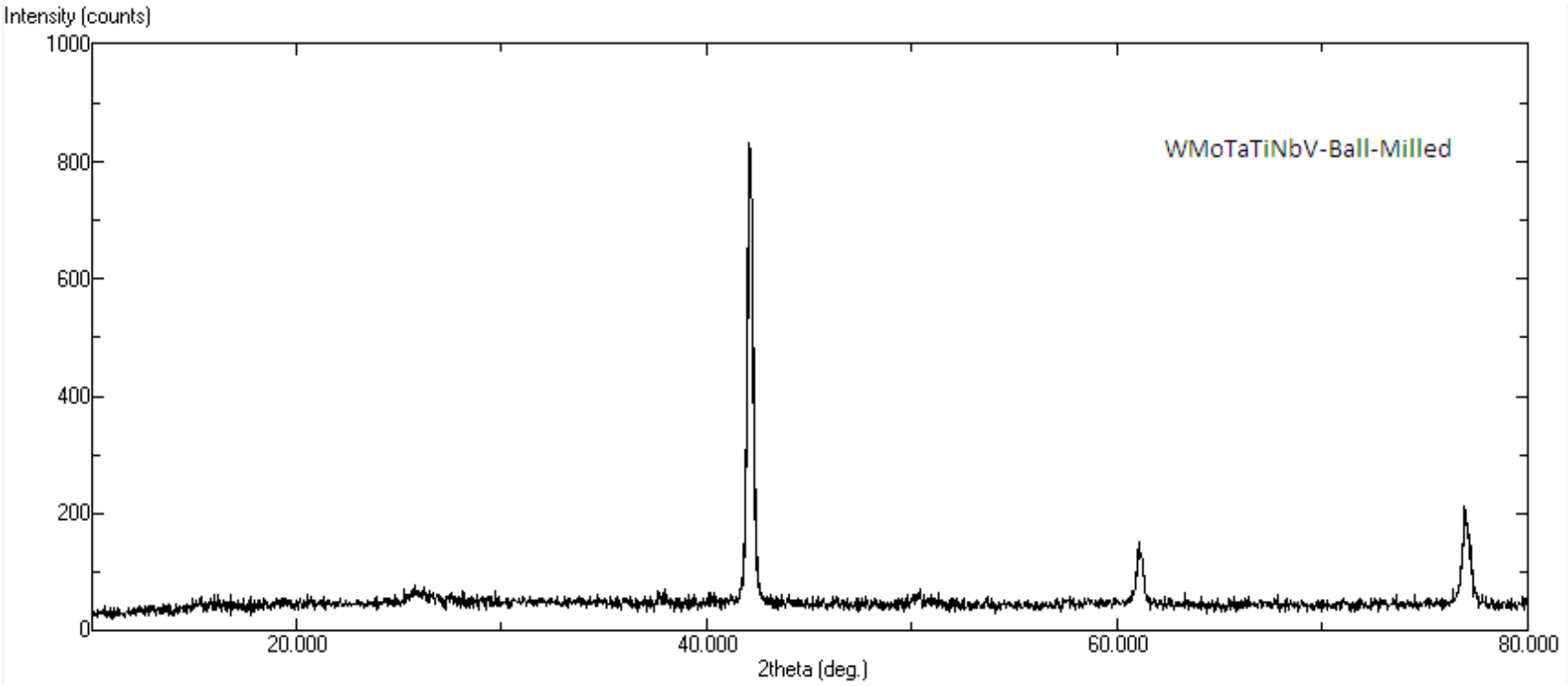



XRD patterns of HfNbTaTiVZr in the (a) pre-melting powder mixture and (b) as-solidified state

# $MoNbTaTiVW/Y_2O_3$

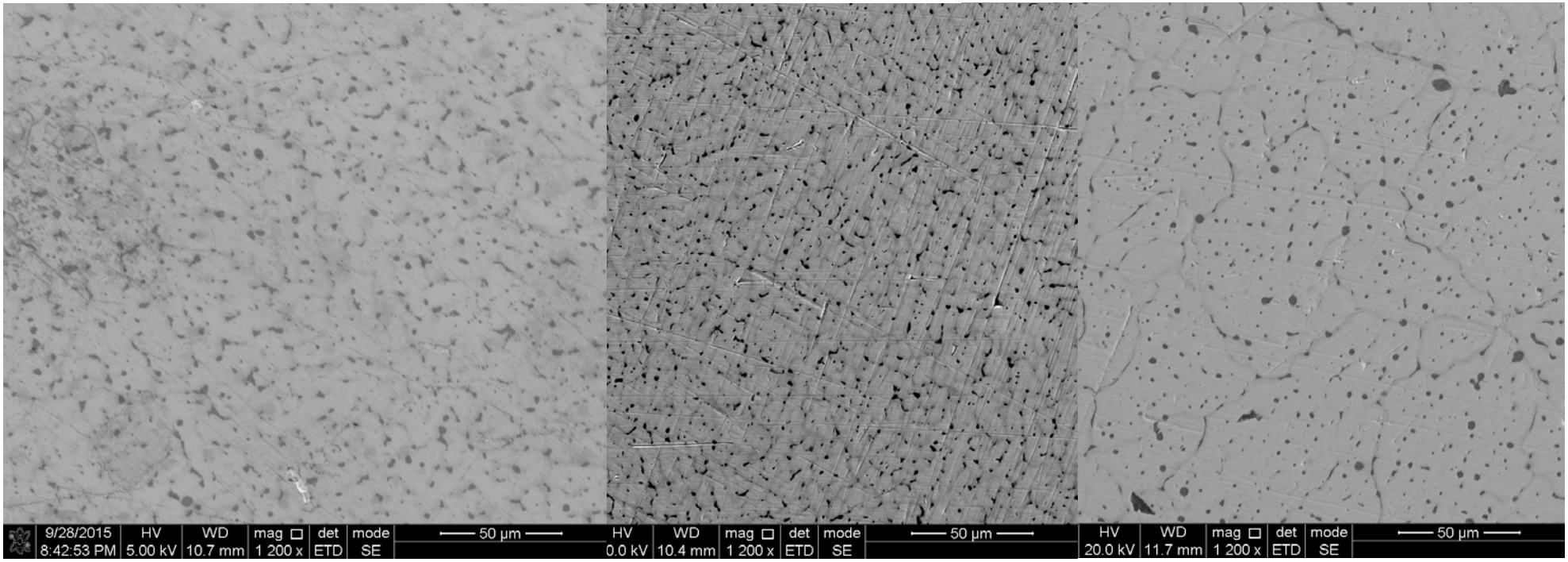


# MoNbTaTiVW

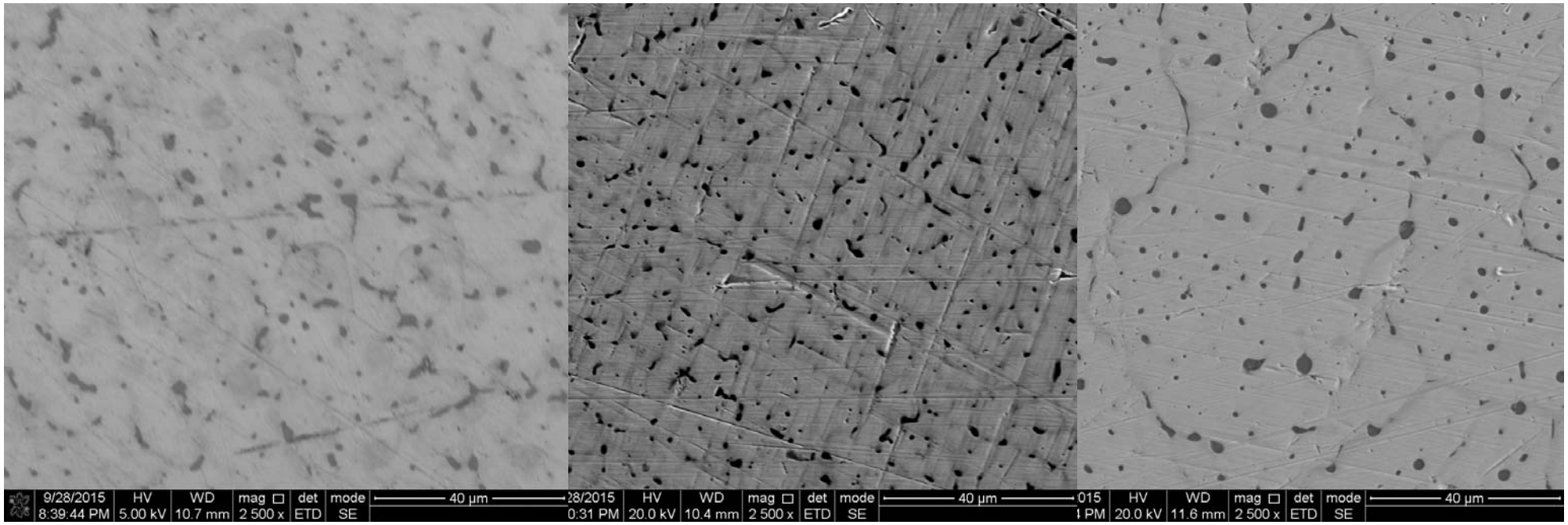

Intensity (counts)
1000
800
600
400
200
0
WMoTaTiNbV-Ball-Milled
20.000
40.000
60.000
80.000
2theta (deg.)

# $Y_2O_3$ Doped Senerary MoNbTaTiVW

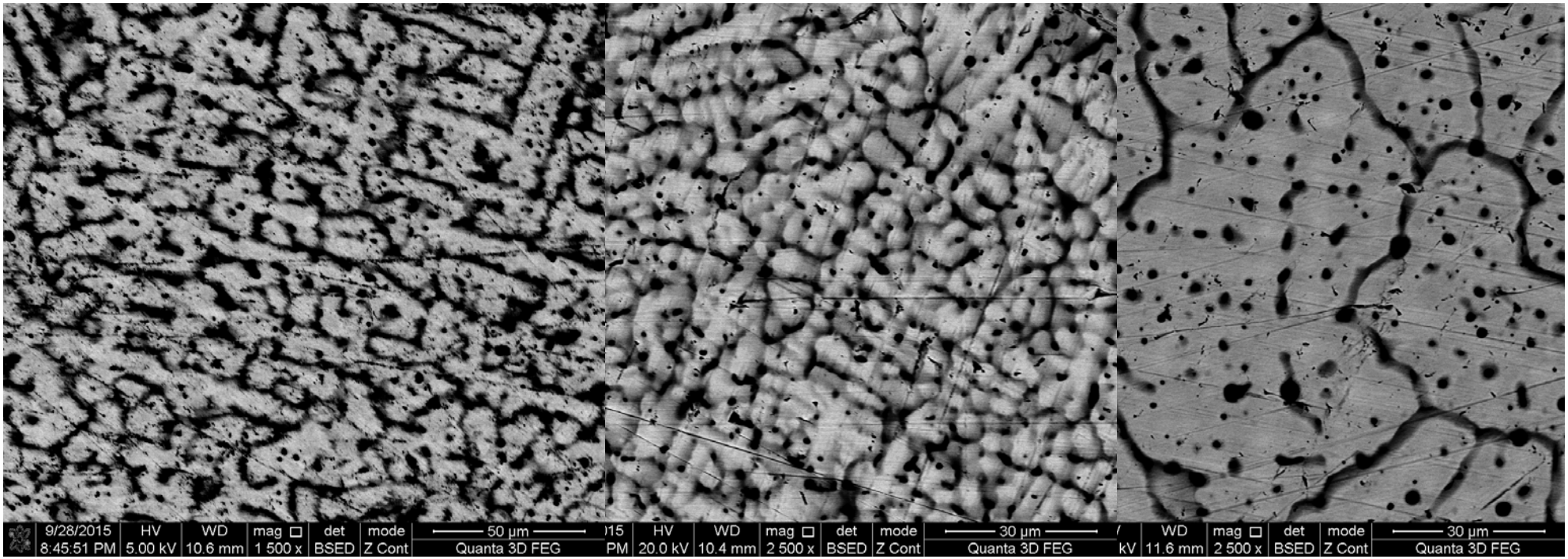
# SEM of HEA doped with $Y_2O_3$ (0.5%, 1.0% and 1.5%)



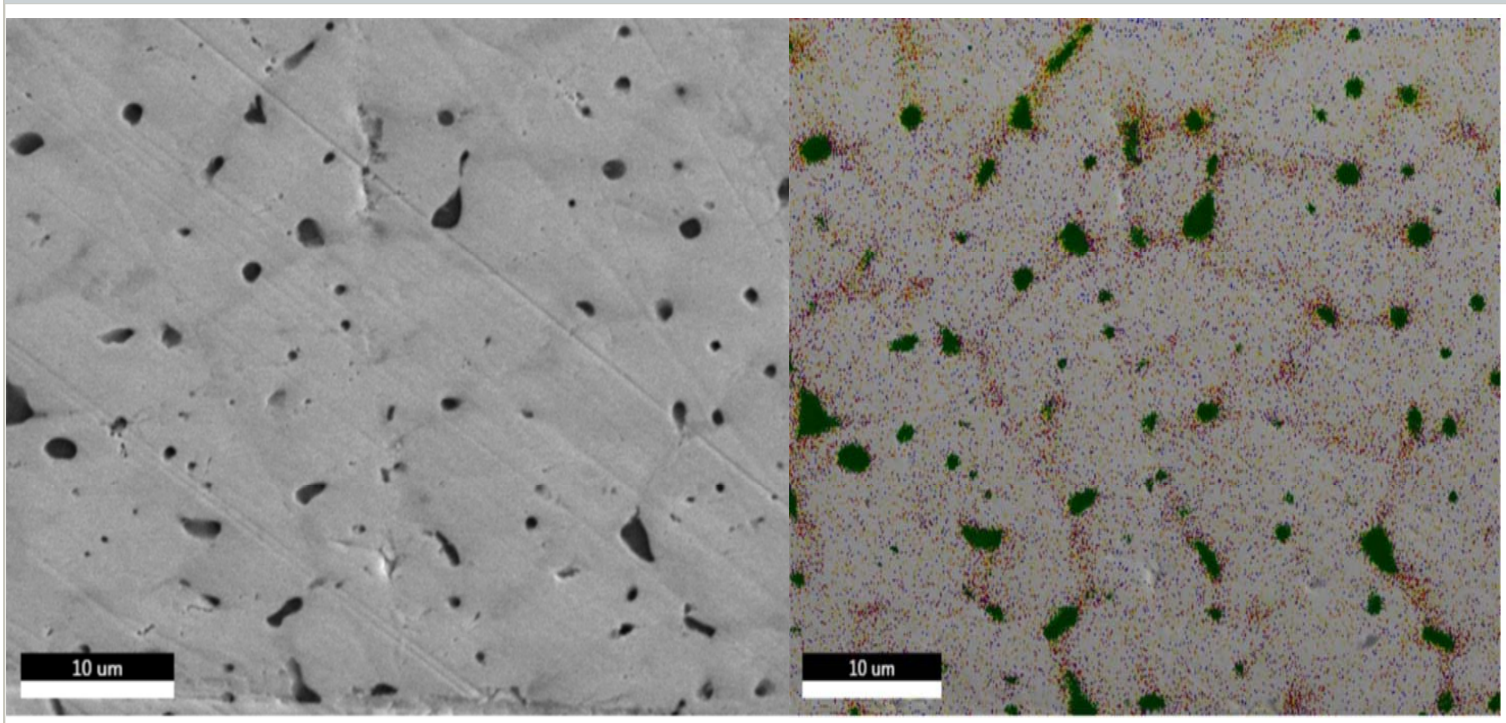
# SEM of HEA doped with $Y_2O_3$ (0.5%, 1.0% and 1.5%)



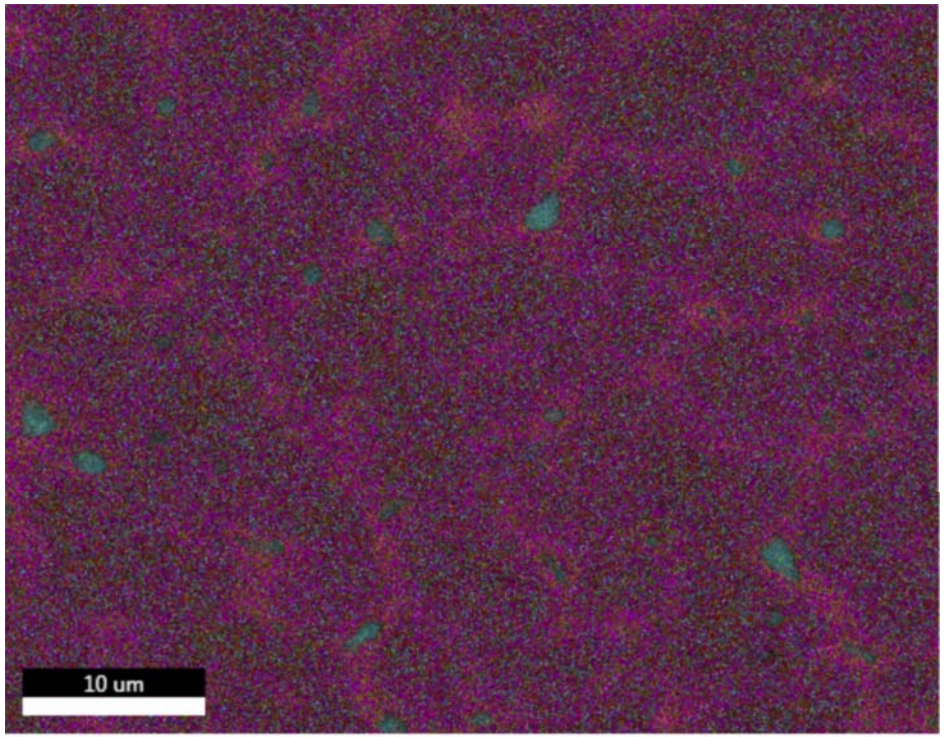
# Quanta 3D FEG (0.5%, 1.0%, and 1.5%)



# EDAX TEAM 0.5% $Y_2O_3$



# EDAX Element overlay




4% O K

4% Y L

15% NbL

21% MoL

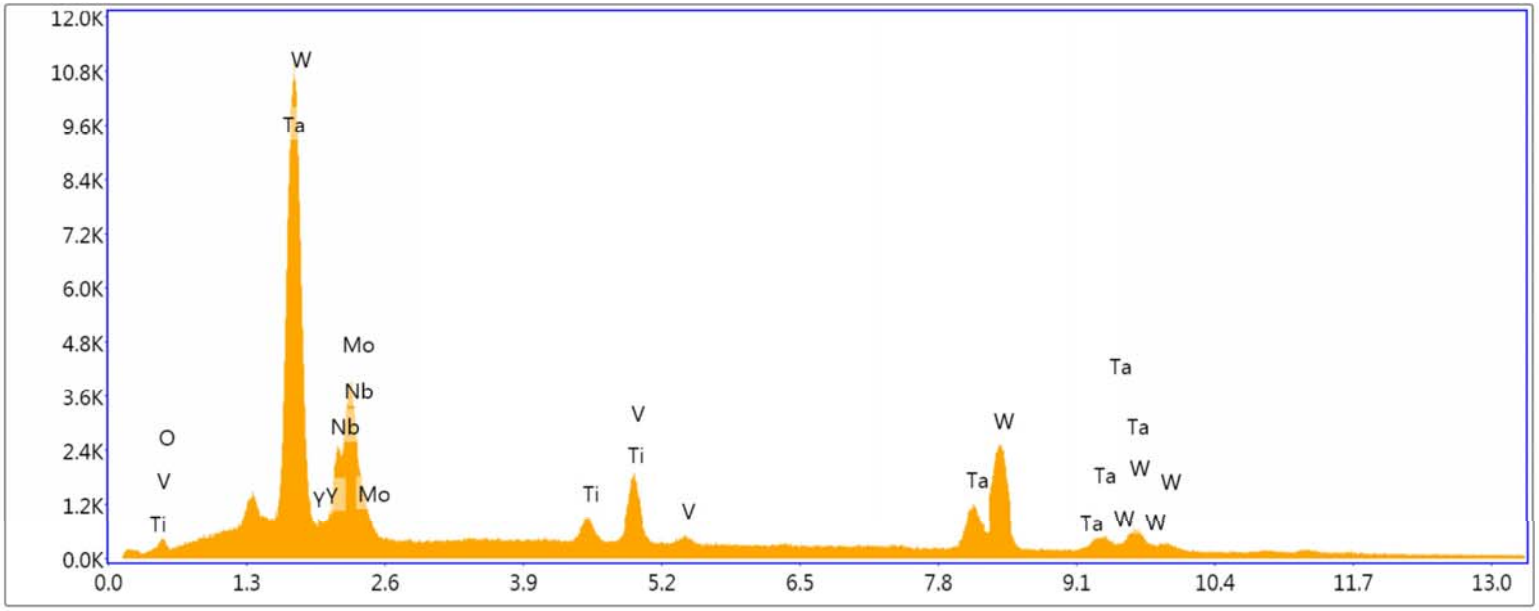
12% TiK

17% V K

13% TaL

14% W L

# Phase Analysis

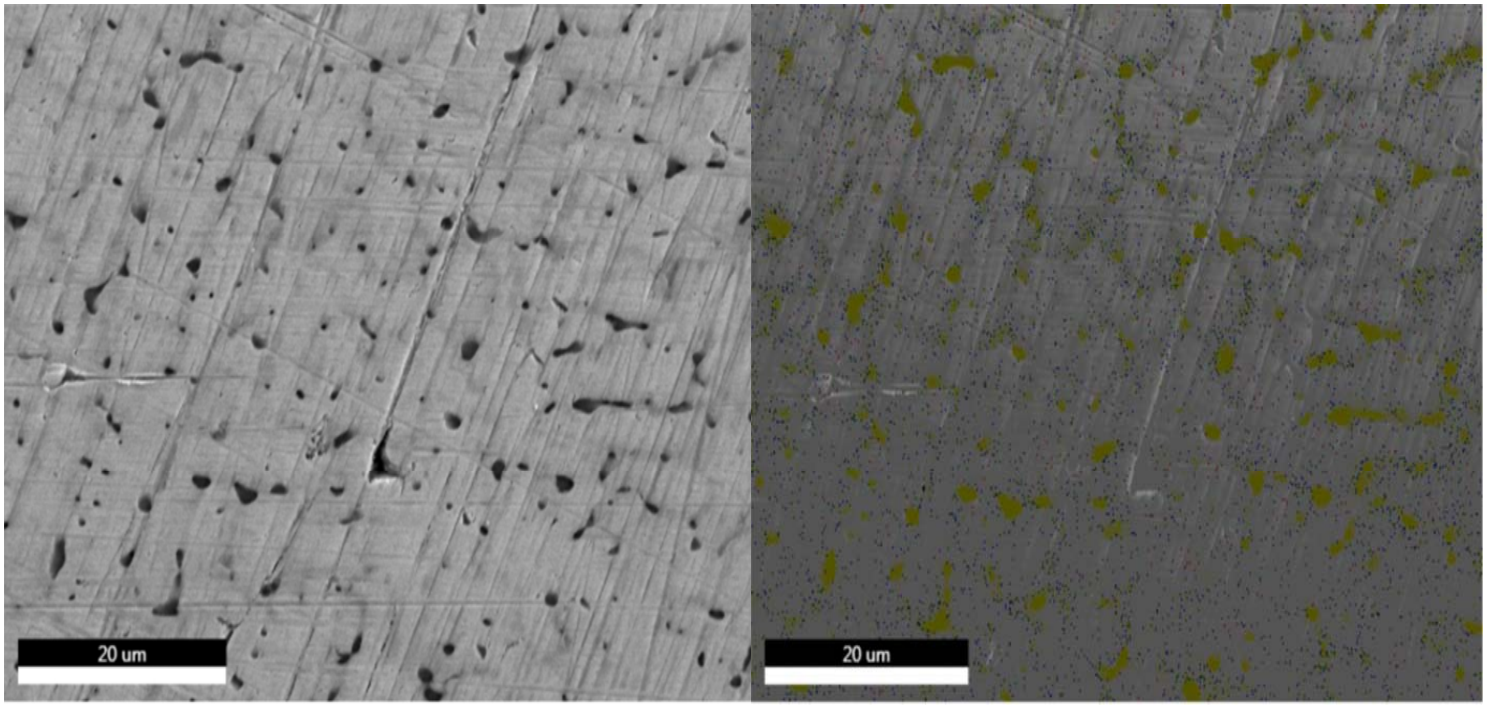



Lsec: 11.9 0 Cnts 0.000 keV Det: Apollo XL-SDD Det

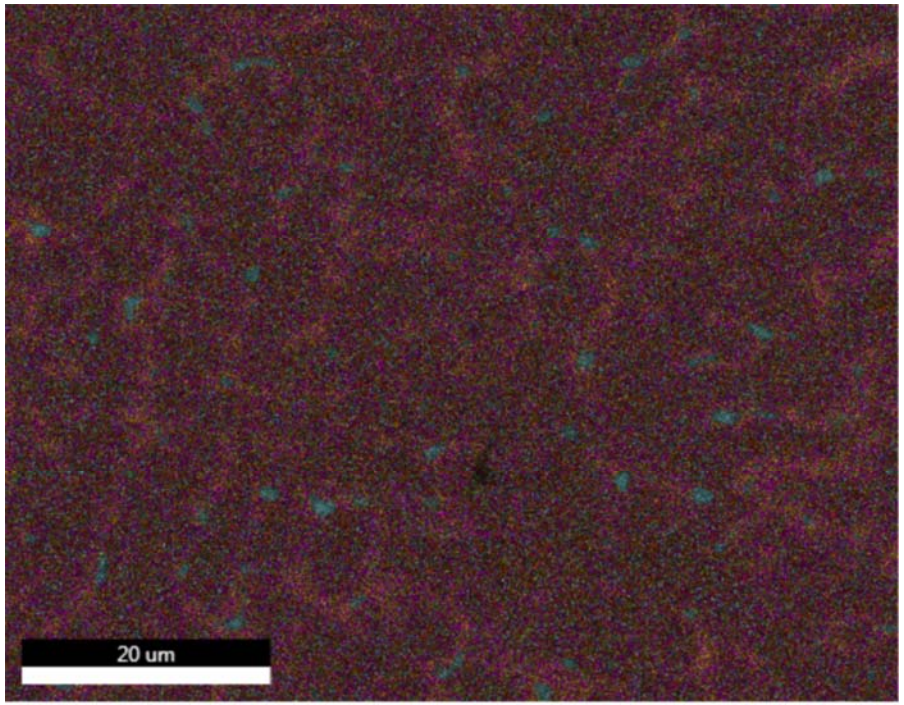
# eZAF Smart Quant Results

| Element | Weight % | Atomic % | Net Int. | Error % | Kratio | Z | R | A | F |
|---|---|---|---|---|---|---|---|---|---|
| O K | 1.45 | 10.76 | 104.70 | 18.64 | 0.0031 | 1.5396 | 0.7190 | 0.1388 | 1.0000 |
| Y L | 0.50 | 0.67 | 85.60 | 27.08 | 0.0027 | 1.0952 | 0.9167 | 0.4797 | 1.0141 |
| NbL | 8.68 | 11.10 | 1560.80 | 8.97 | 0.0492 | 1.0971 | 0.9281 | 0.5085 | 1.0160 |
| MoL | 13.15 | 16.29 | 2309.10 | 8.38 | 0.0726 | 1.0861 | 0.9336 | 0.5001 | 1.0159 |
| TiK | 1.73 | 4.28 | 614.40 | 9.07 | 0.0175 | 1.2354 | 0.8393 | 0.7707 | 1.0625 |
| V K | 5.10 | 11.90 | 1613.80 | 5.48 | 0.0544 | 1.2094 | 0.8477 | 0.8156 | 1.0814 |
| TaL | 16.02 | 10.52 | 1329.80 | 6.88 | 0.1831 | 0.9284 | 1.0376 | 1.0043 | 1.2258 |
| W L | 53.37 | 34.49 | 3310.60 | 4.81 | 0.5405 | 0.9223 | 1.0376 | 1.0050 | 1.0925 |

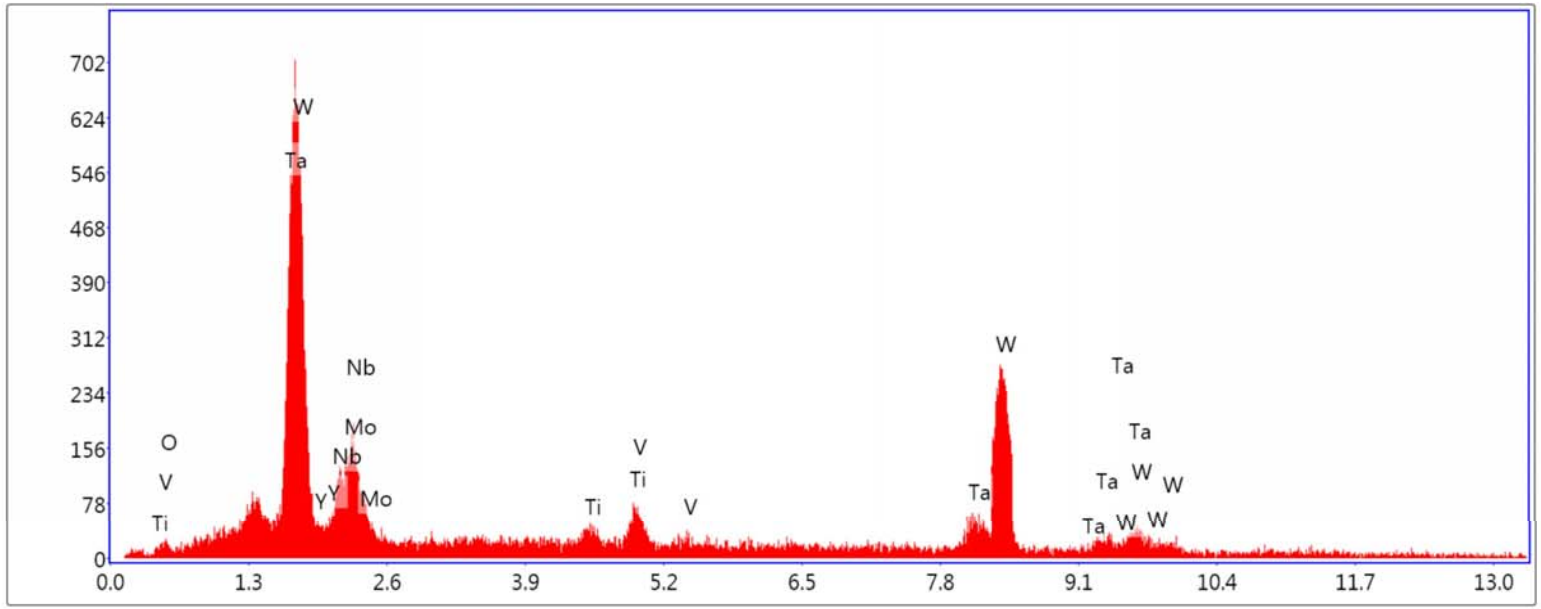
# EDAX TEAM 1.0% $Y_2O_3$



# EDAX Element overlay



# Phase Analysis

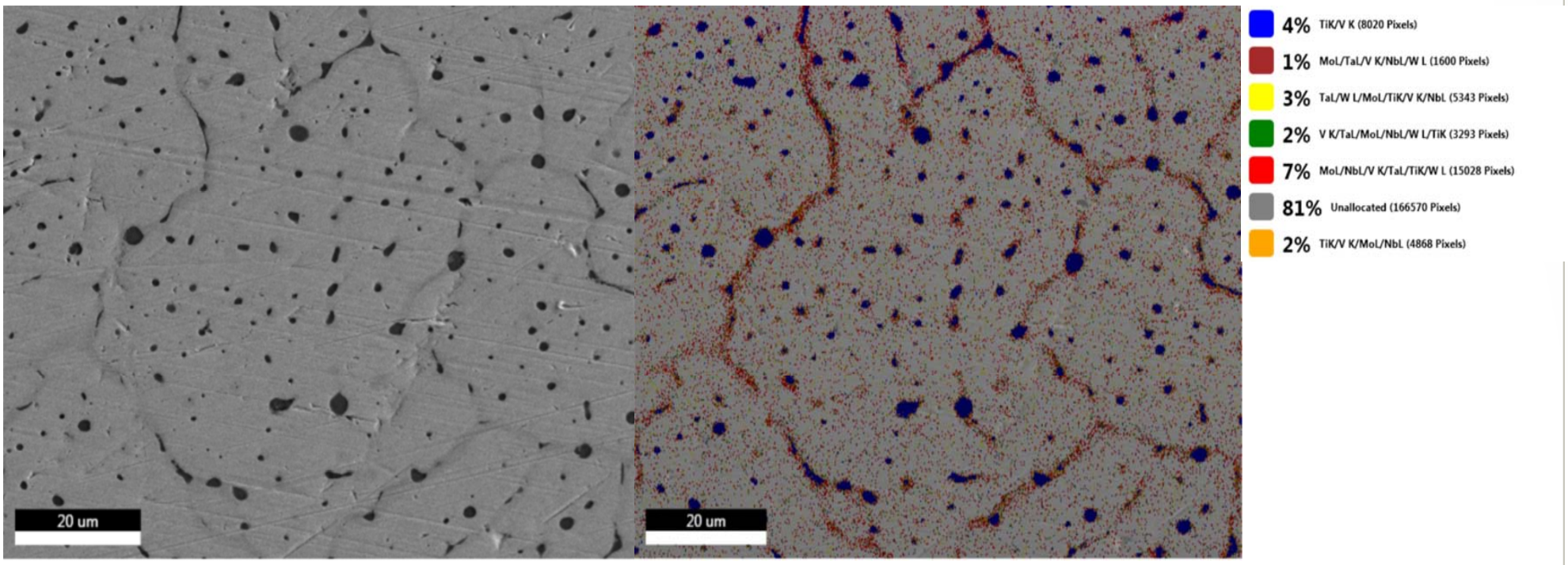



Lsec: 0.7 0 Cnts 0.000 keV Det: Apollo XL-SDD Det

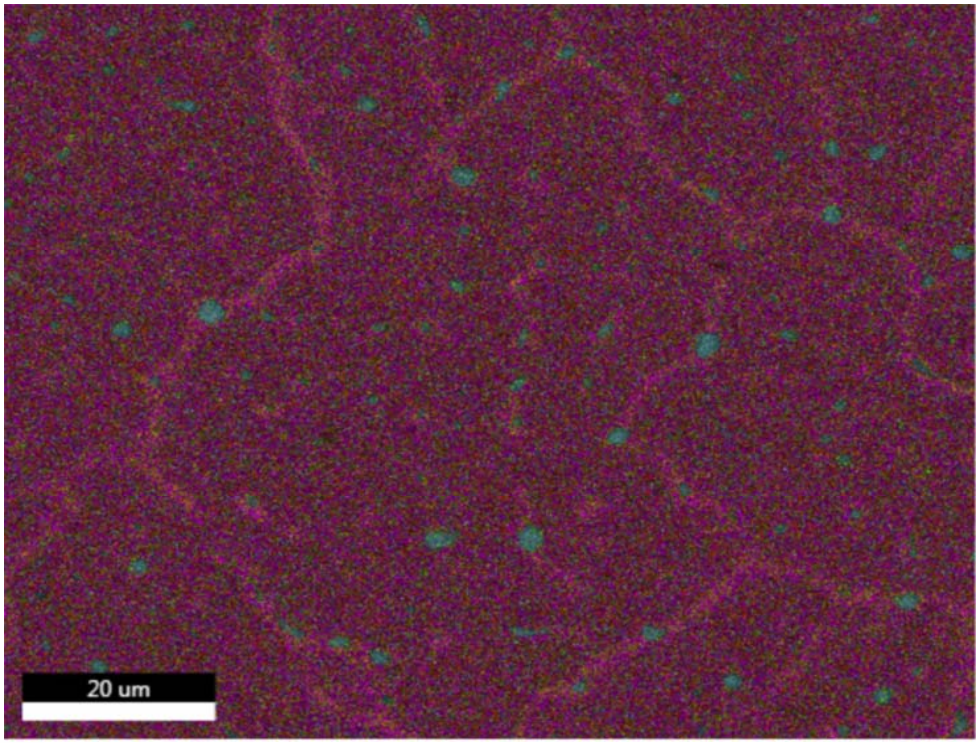
# eZAF Smart Quant Results

| Element | Weight % | Atomic % | Net Int. | Error % | Kratio | Z | R | A | F |
|---|---|---|---|---|---|---|---|---|---|
| O K | 0.81 | 7.13 | 87.30 | 74.37 | 0.0020 | 1.5817 | 0.7005 | 0.1532 | 1.0000 |
| Y L | 0.89 | 1.40 | 184.60 | 58.39 | 0.0044 | 1.1231 | 0.8924 | 0.4354 | 1.0128 |
| NbL | 5.92 | 8.96 | 1286.20 | 14.33 | 0.0309 | 1.1251 | 0.9036 | 0.4569 | 1.0158 |
| MoL | 7.14 | 10.47 | 1516.10 | 14.64 | 0.0363 | 1.1138 | 0.9091 | 0.4488 | 1.0170 |
| TiK | 0.91 | 2.67 | 432.20 | 28.92 | 0.0093 | 1.2680 | 0.8188 | 0.7572 | 1.0702 |
| V K | 2.36 | 6.51 | 1003.60 | 21.49 | 0.0258 | 1.2417 | 0.8274 | 0.8038 | 1.0942 |
| TaL | 9.60 | 7.47 | 1159.80 | 21.88 | 0.1215 | 0.9596 | 1.0210 | 1.0021 | 1.3160 |
| W L | 72.38 | 55.39 | 6084.20 | 9.04 | 0.7559 | 0.9540 | 1.0218 | 1.0032 | 1.0911 |

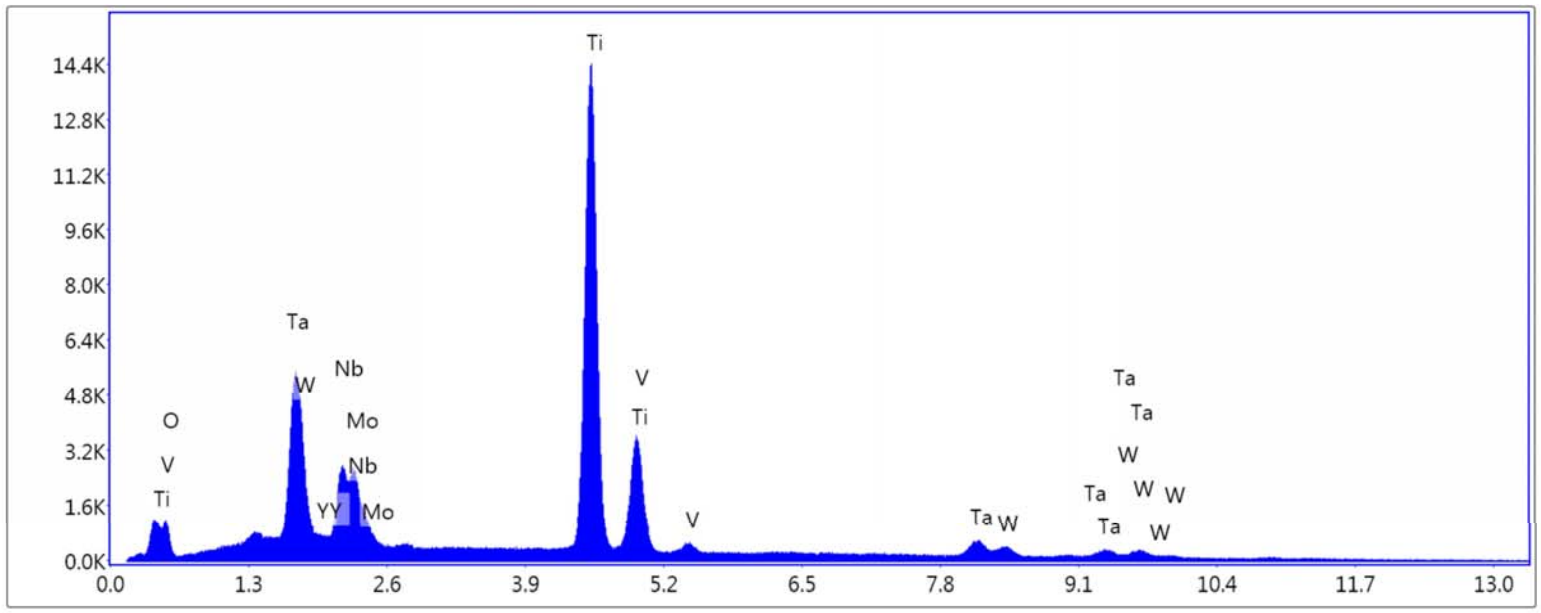
# EDAX TEAM 1.5% $Y_2O_3$



# EDAX Element overlay




# Phase Analysis




Lsec: 16.0 0 Cnts 0.000 keV Det: Apollo XL-SDD Det

# eZAF Smart Quant Results

| Element | Weight % | Atomic % | Net Int. | Error % | Kratio | Z | R | A | F |
|---|---|---|---|---|---|---|---|---|---|
| O K | 13.87 | 38.88 | 405.00 | 12.39 | 0.0169 | 1.2889 | 0.8529 | 0.0945 | 1.0000 |
| Y L | 0.00 | 0.00 | 0.00 | 99.99 | 0.0000 | 0.9187 | 1.0804 | 0.7402 | 1.0206 |
| NbL | 7.08 | 3.42 | 1210.90 | 5.30 | 0.0536 | 0.9197 | 1.0917 | 0.8039 | 1.0228 |
| MoL | 4.35 | 2.03 | 743.10 | 5.49 | 0.0328 | 0.9102 | 1.0972 | 0.8081 | 1.0249 |
| TiK | 47.47 | 44.46 | 11540.60 | 2.40 | 0.4620 | 1.0273 | 0.9712 | 0.9204 | 1.0291 |
| V K | 7.11 | 6.26 | 1446.90 | 3.72 | 0.0688 | 1.0035 | 0.9775 | 0.9293 | 1.0364 |
| TaL | 11.25 | 2.79 | 491.40 | 9.85 | 0.0953 | 0.7417 | 1.1396 | 1.0133 | 1.1272 |
| W L | 8.86 | 2.16 | 316.50 | 13.86 | 0.0728 | 0.7339 | 1.1342 | 1.0145 | 1.1026 |

# Hardness Measurement Results

- HEA doped with 0.5% $Y_2O_3$

  Hardness (GPa): 5.01

- HEA doped with 1.0% $Y_2O_3$

  Hardness (GPa): 4.99

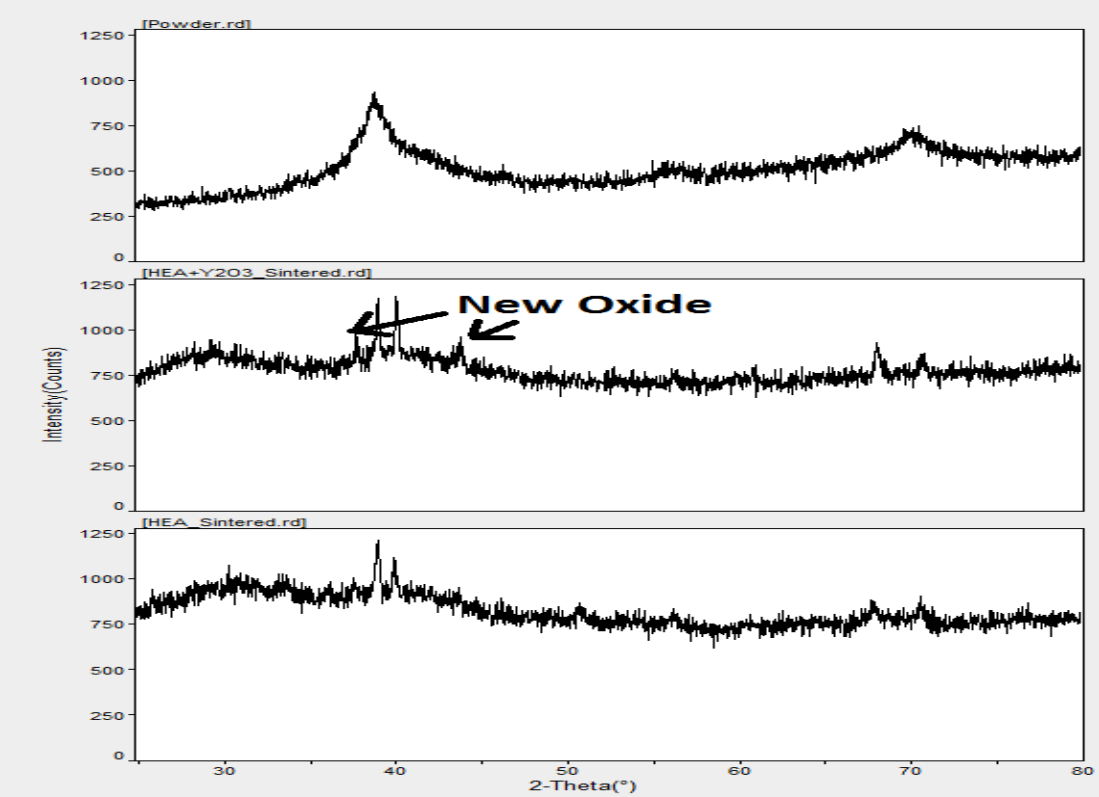
- HEA doped with 1.5% $Y_2O_3$

  Hardness (GPa): 5.58

# $Y_2O_3$ Doped MoNbTaVW

- 4 wt% $Y_2O_3$ (< 5μm) doped MoNbTaVW (BCC structure) was mixed, ball milled, and pressed in 1/8 inch die, then sintered under 1,400 °C in Ar environment for 90 minutes.
- The raw HEA powder (~ 15 μm) was stored in HPC lab for ~ 2 years. The BCC structure is still explicitly shown.
- New $YMO_x$ type oxide were shown in the $Y_2O_3$ Doped MoNbTaVW.
- Further comparison experiment: new samples with SEM/EDS observation is ongoing.

# $Y_2O_3$ Doped MoNbTaVW




# Publication and Awards

1. Paper published:

- "Senary refractory high entry alloy HfNbTaTiVZr", M. Gao, B. Zhang, S. Yang, and S. Guo, Matallurgical and Materials Transactions A, Symposium: High Entropy Alloys III, pp 1-13, 2015.
- "Senary refractory high entry alloy MoNbTaTiVW", B. Zhang, M. Gao, Y. Zhang, S. Yang, and S. Guo, Materials Science and Technology **31**, 1207 (2015).
- "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:

- "Elastic and thermal dynamic properties of MoNbTaVW", Y. Yang, L. Chilla, B. Zhang, S. Guo, E. Khosravi, S. Yang, G. Li, P. Mensah, H. Jerro, S. Ibekwe, and G. Joshi, NSF CIMM Annual Meeting, Baton Rouge, Louisiana, April 8, 2016.
- "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 – 8/31/2016 (PI: Guo, Co-PI: Yang).
- NSF-CIMM, Consortium for Innovation in Manufacturing and Materials, HPC team has been working on laser 3D printing HEA design and validation (dislocation dynamics related creep & fatigue) and electrical transportation properties. A five year six LA research universities joint project. Award # OIA-1541079 with total $20 M from 10/1/2015 ~ 9/30/2020.

# 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 Support: Jessica Mullen, Steven Markovich, and Bethan Young.
- Graduate students: Boliang Zhang, Yi Zhang, Lokeshwar Chilla, Yan Yang, 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, Y. Dong, D. Cao, P. Liew, E. Khosravi, J. Yan, and B. Chen.
- LONI Institute and LSU CCT for supercomputer time and internal support.
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# Acknowledgement


SU CS Department & IBM

BERKELEY LAB

Dr. J. Yan

HPSTAR 高压先进科研中心 HIGH PRESSURE SCIENCE & TECHNOLOGY ADVANCED RESEARCH

Dr. B. Chen

LSU

Drs. Y. Dong, S. Guo, D. Cao, & G. Li
Students: B. Zhang & Y. Zhang