Directed Vapor Technologies International, Inc.

DOE SBIR Phase II: Grant No. DE- SC0013098

Advanced Bond Coats for Thermal Barrier Coating Systems Based on High Entropy Alloys

Program Partners: Brian Gleeson, U. Pitt. and Fan Zhang, Computherm

Program Manager: Seth Lawson, DOE

Outline:

- DVTI Overview
- Directed Vapor Deposition Approach
- TBC Systems Using DVD Deposition
- High Entropy Alloys (HEA)
- High Entropy Alloys as Bond Coats for TBC systems
- Quasi-Combinatorial HEA Development
- Computational Techniques for HEA Bond Coat Optimization
- Next Steps

CompuTherm FOR MATERIALS DESIGN

Company Overview

Core Competencies / Expertise:

- Directed Vapor Deposition (DVD) – a modified Electron Beam Physical Vapor Deposition process
- High Rate Deposition for low cost manufacturing
- Non-Line-Of-Sight (NLOS) capabilities for parts with complex geometries, internal surfaces and wires / fibers.
- Application of advanced coatings and specialty coatings

Production Capabilities:

- Modern coating facility
- Production coating capability
  - 75Kv Electron Beam DVD equipment designed, built and installed by DVTI
  - Continuous Fiber Handling Equipment
  - Trained and experienced staff
  - Post coating characterization
- ISO 9001:2015 Registered

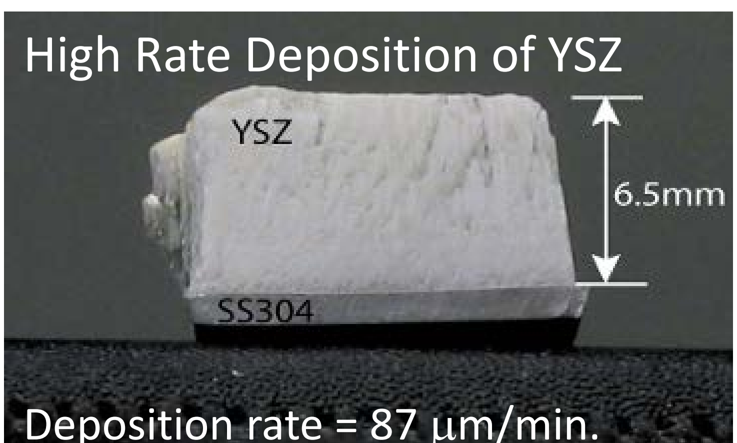
Directed Vapor Deposition

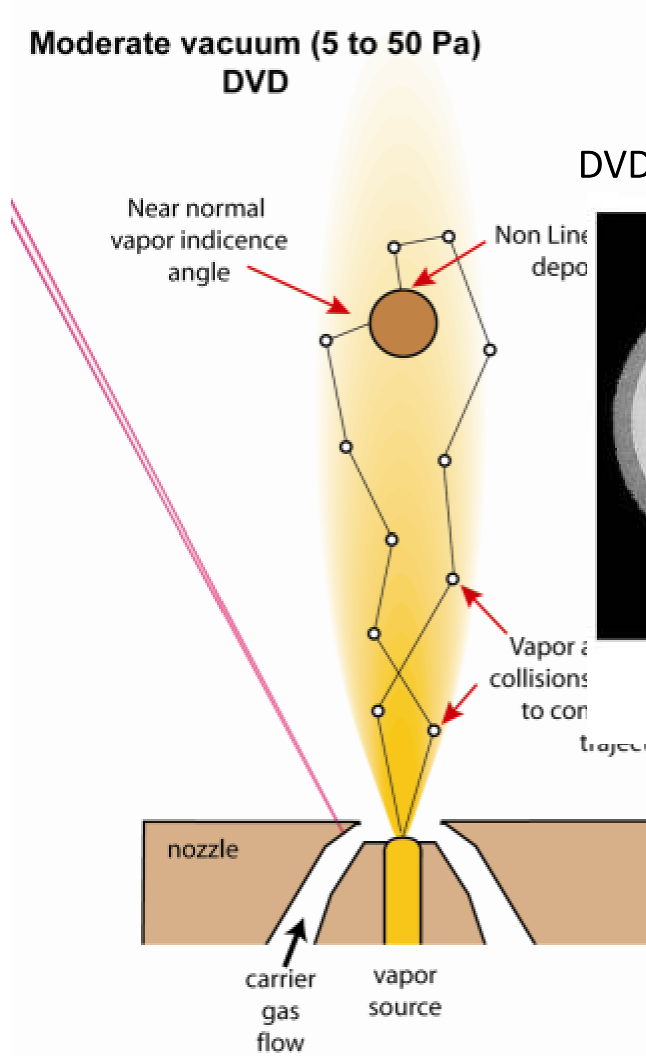
Concept

gas phase scattering of an evaporated vapor flux (by collisions with supersonic gas) enables the flux trajectory to be controlled

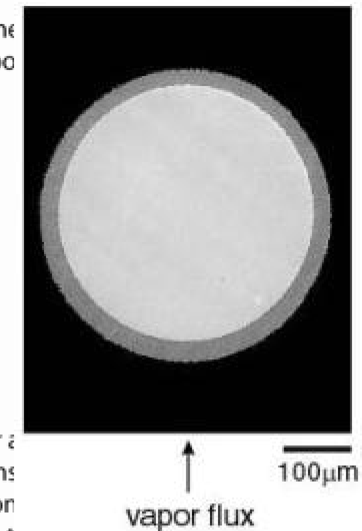
Rationale for DVD:

- increase deposition efficiency of EB-PVD process
- increase deposition rate
- non-line-of-sight coating
- composition and morphology control
- soft vacuum – ease of use





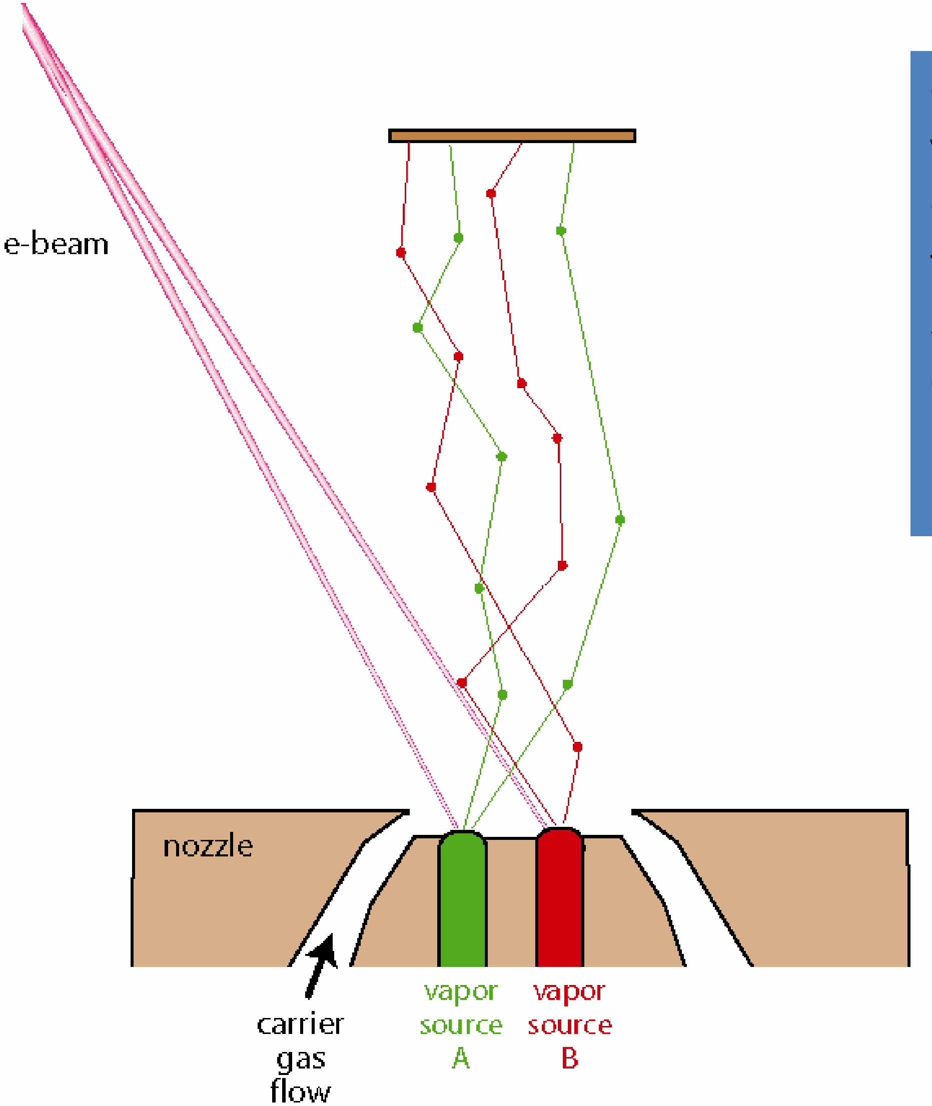
DVD Coated Wire



DVD Advantages:

- Non Line-of-sight capability
- High deposition efficiency

Directed Vapor Deposition

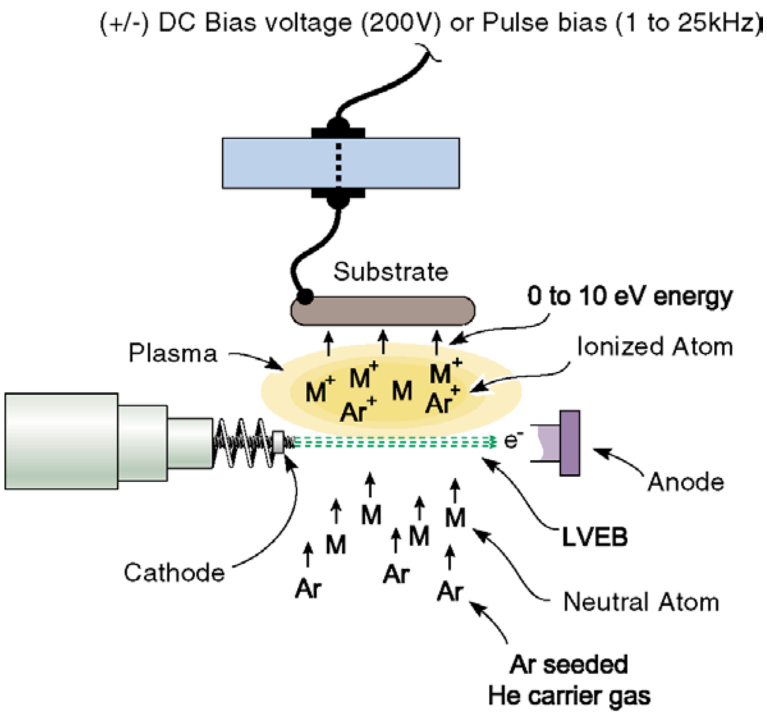


Multi-Source Evaporation

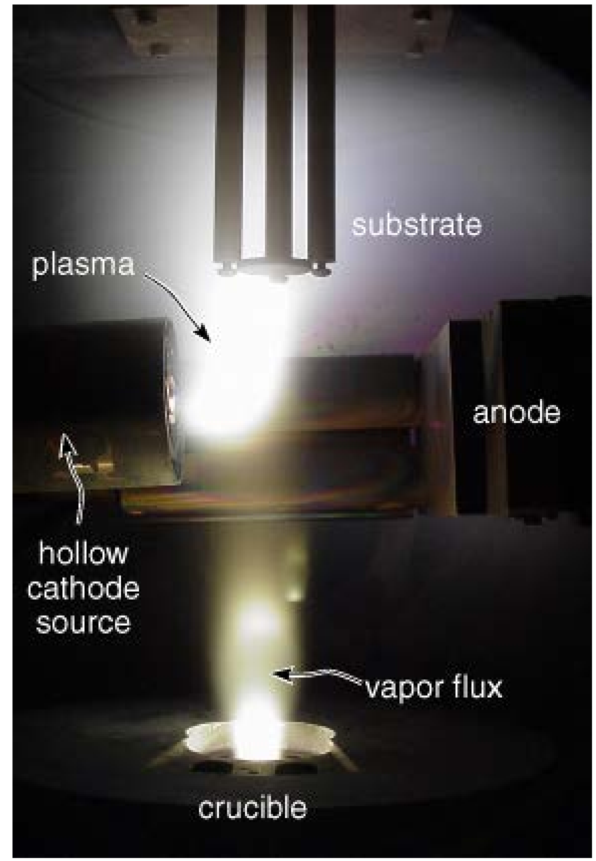
- vapor phase collisions improve vapor flux intermixing
- high deposition efficiency enable the use of relatively small diameter source rods (while retaining good deposition rates). These can be placed in close proximity to further promote vapor flux intermixing.

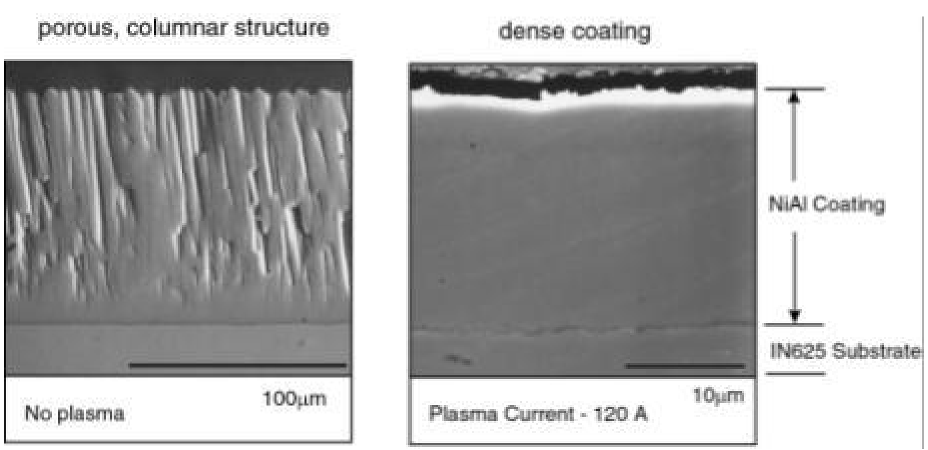
Enables deposition of multi-component materials with large vapor pressures differences and multilayered coatings

Processing Approach



Multi-source DVD with Plasma Activation

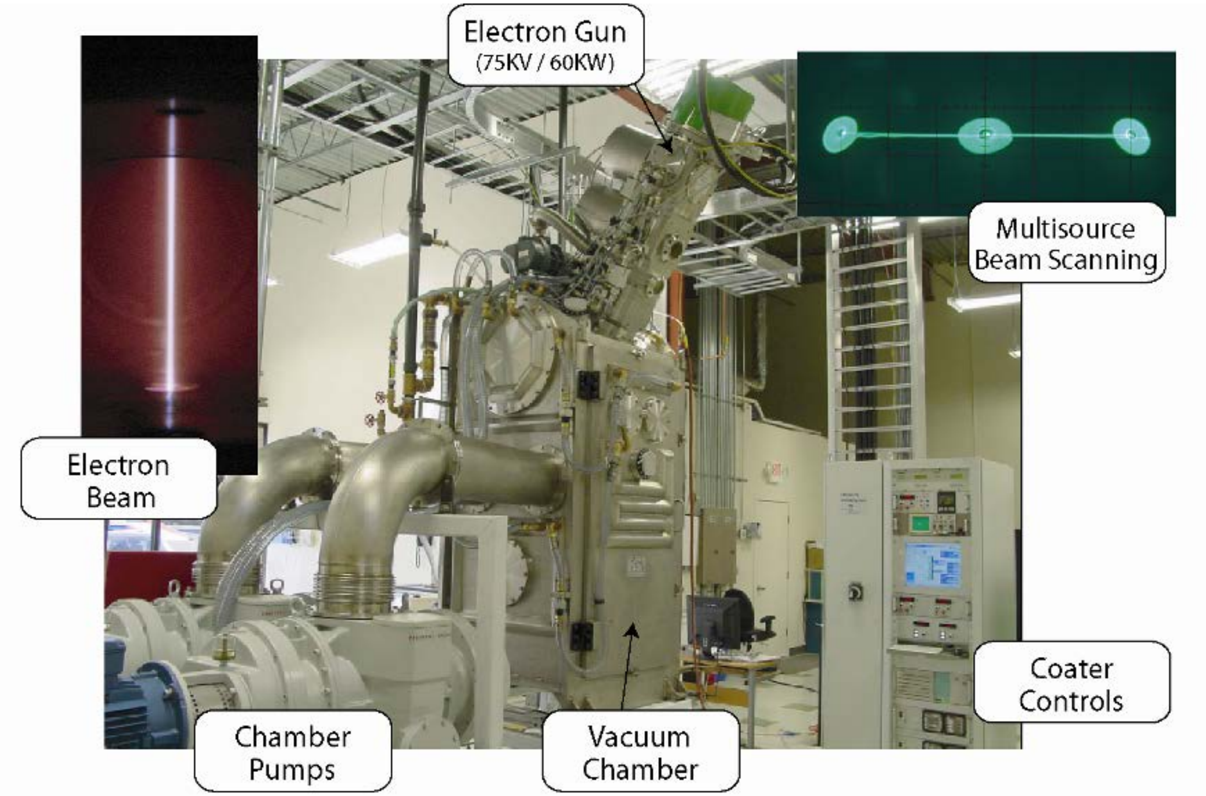




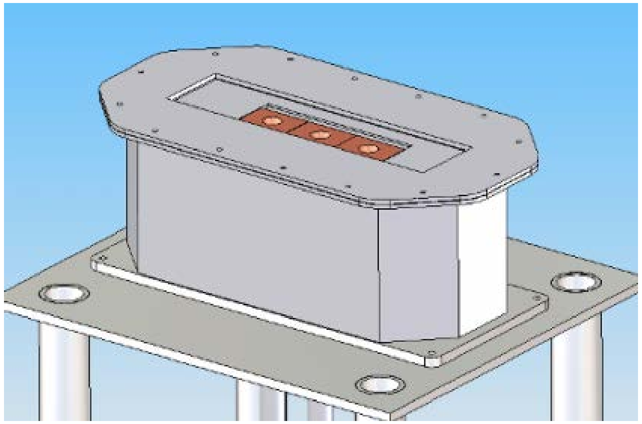
No plasma 100µm

Plasma Current - 120 A 10µm

Production Scale DVD Coater

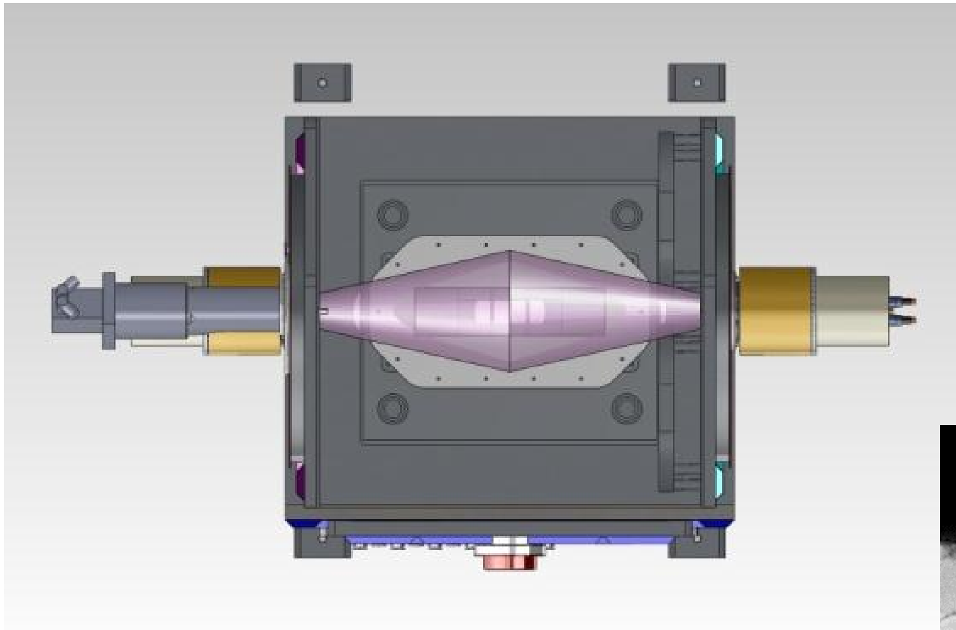


- Crucible sizes up to 1.75" for high rate deposition
- Scaled coating zone for large area deposition
- Full scale plasma activation enables high energy deposition across entire coating zone

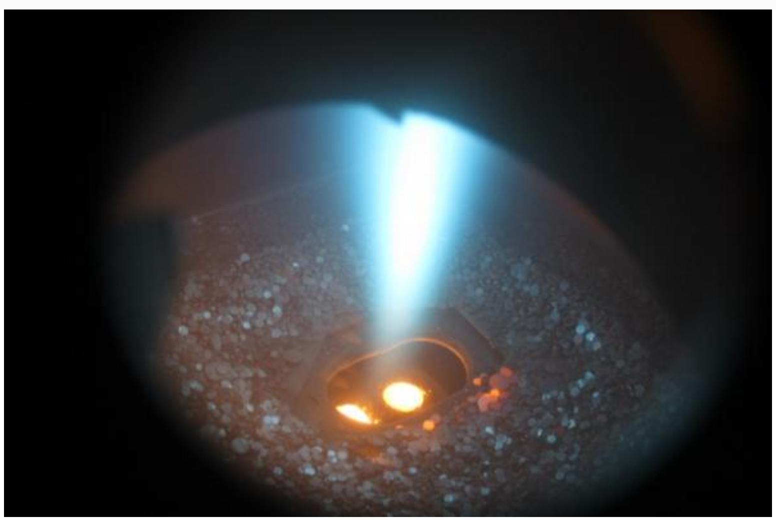


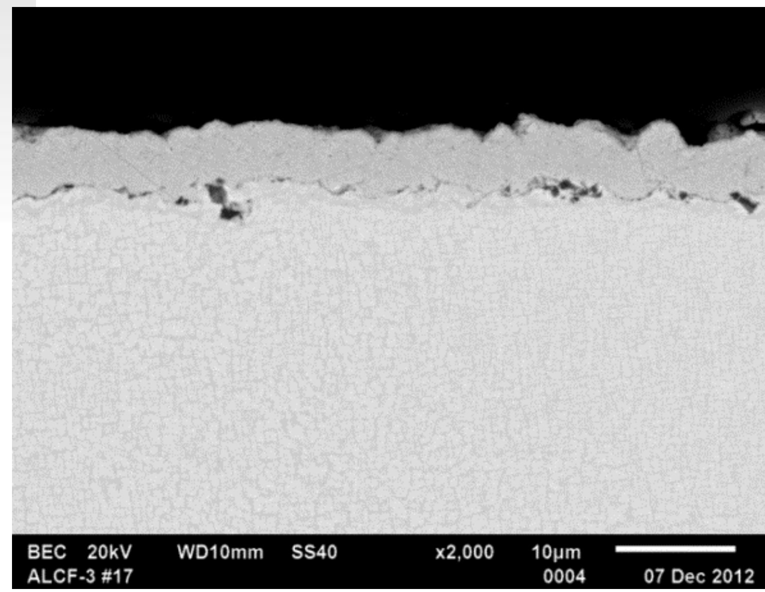
- Coating equipment designed for coated turbine disks, vanes and blades (metal and ceramic coatings)
- Compatible with other aerospace components (landing gear, actuators, fasteners)

DVD - Full Scale Plasma Activation

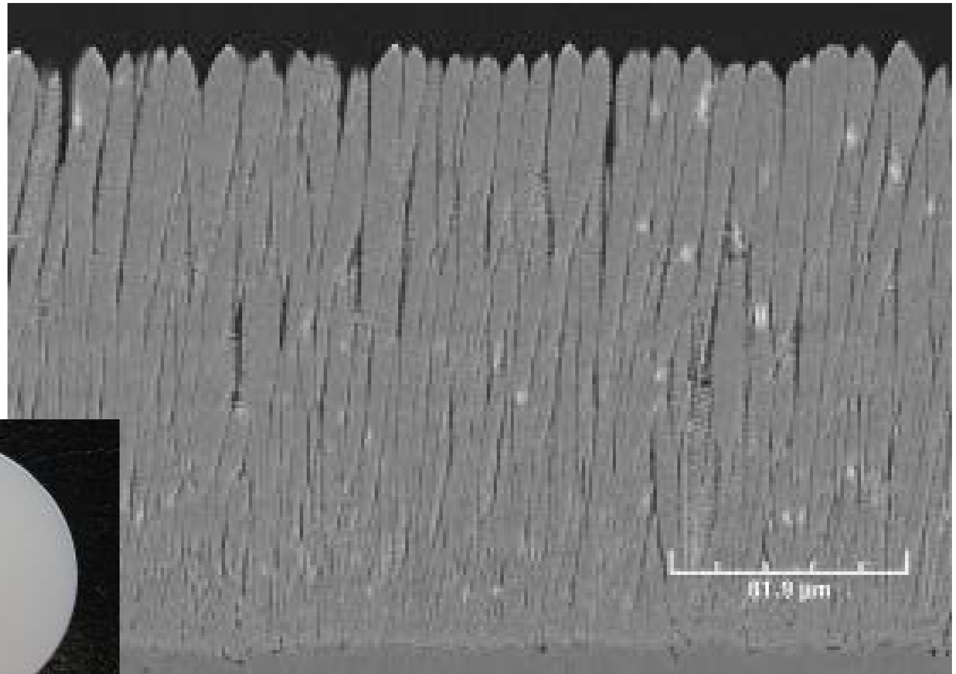


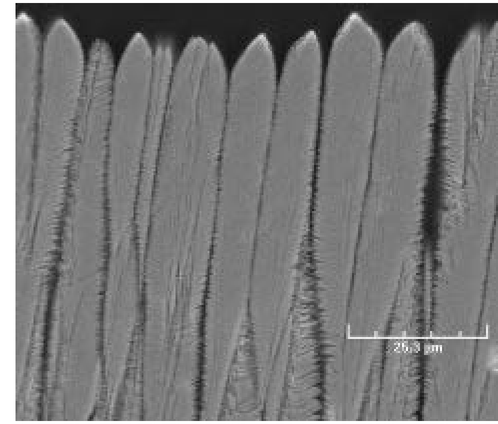
- This system uses a pair of plasma emitters coupled together in a pulsed mode to provide large area plasma activation of multiple vapor plumes.

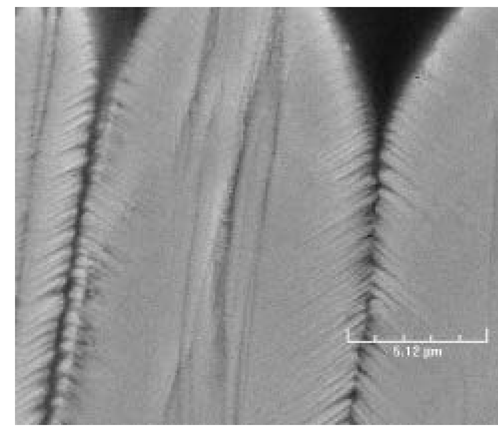




TBC Top Coats







Cyclic Oxidation

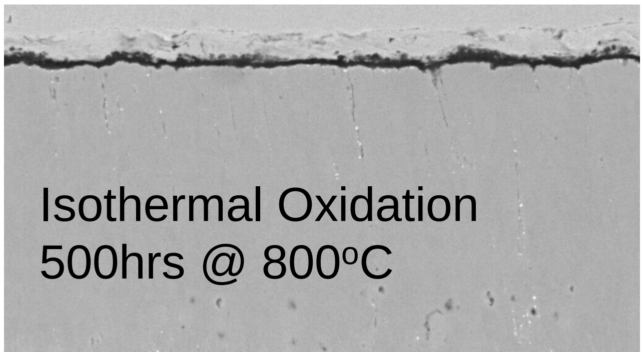
Coating Type	Cycles to Failure
EB-PVD 7 YSZ / CVD PtAl / CMSX-4	1.0X
EB-DVD 7 YSZ / CVD PtAl / CMSX-4	1.5X

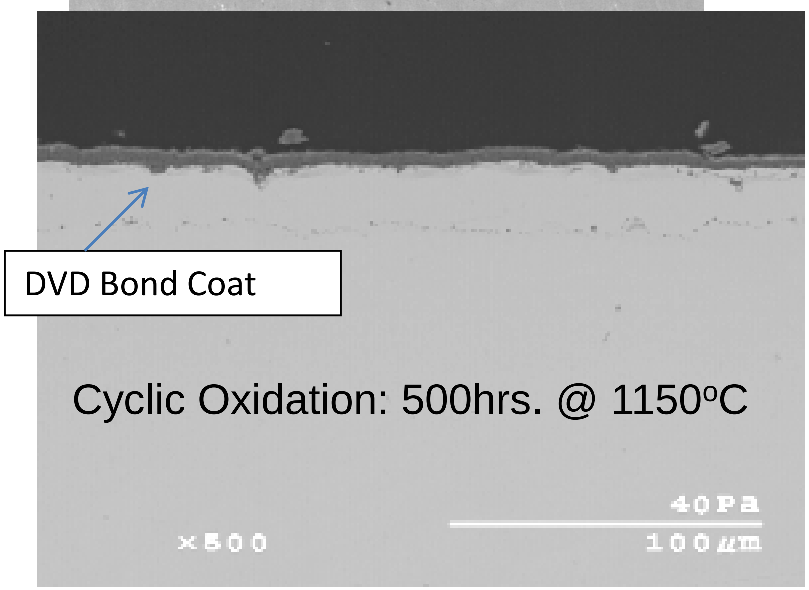
1 hr cycles @ 1120^{o}C

Oxidation and Hot Corrosion Resistance

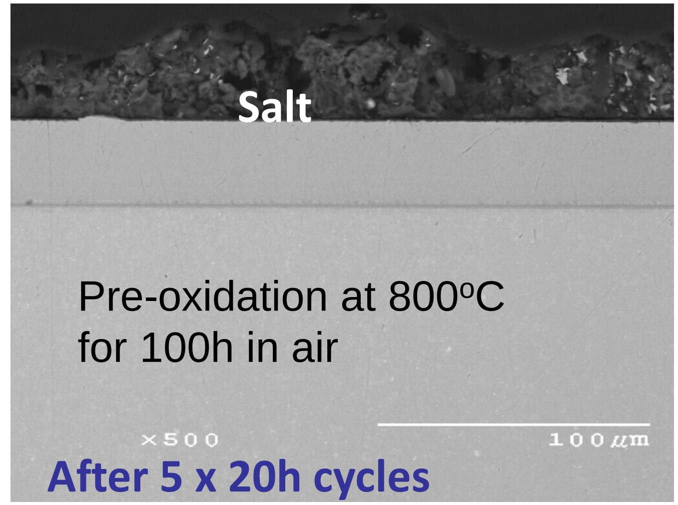
High Temperature Oxidation

Modified NiAl alloys





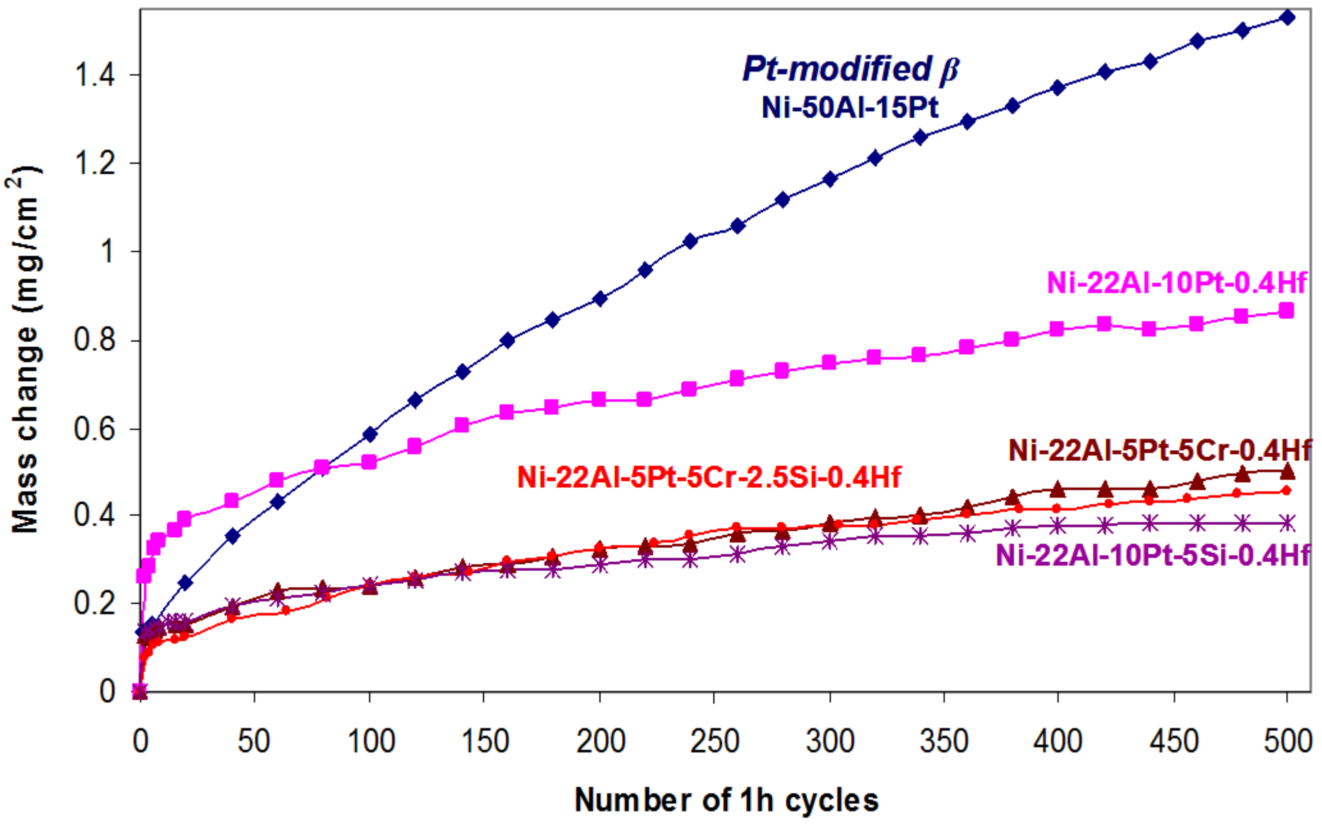
Hot Corrosion Resistance



- Type II Hot corrosion at 700°C
  - Pre-oxidation at 800°C@100hrs in air prior to hot corrosion
  - 1-2 mg/cm_2 Na_2SO_4 was deposited initially and re-deposited between every cycle

Collaboration: Brian Gleeson, U. Pitt.

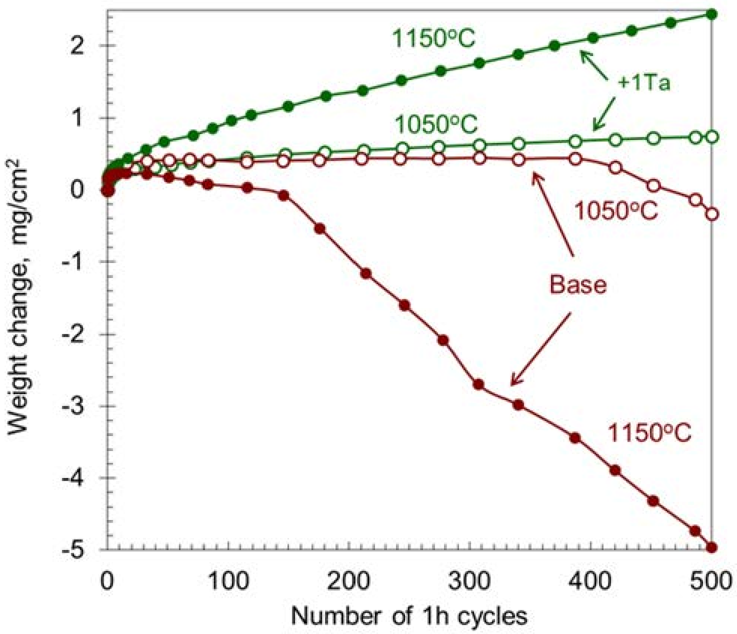
γ/γ' Bond Coats

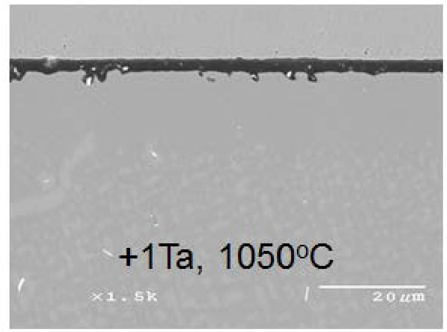


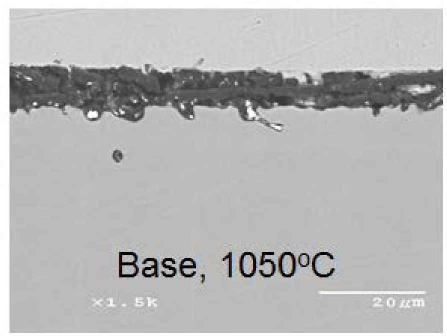
Ta Modified γ/γ' Bond Coats

γ – γ' Alloys with Ta Additions: *Bulk Cyclic Oxidation Kinetics*

• Gleeson / USAF have developed precipitation strengthenable γ-γ' alloys which not only provide enhanced oxidation protection, Such coatings are a potential damping enhanced bond coat.





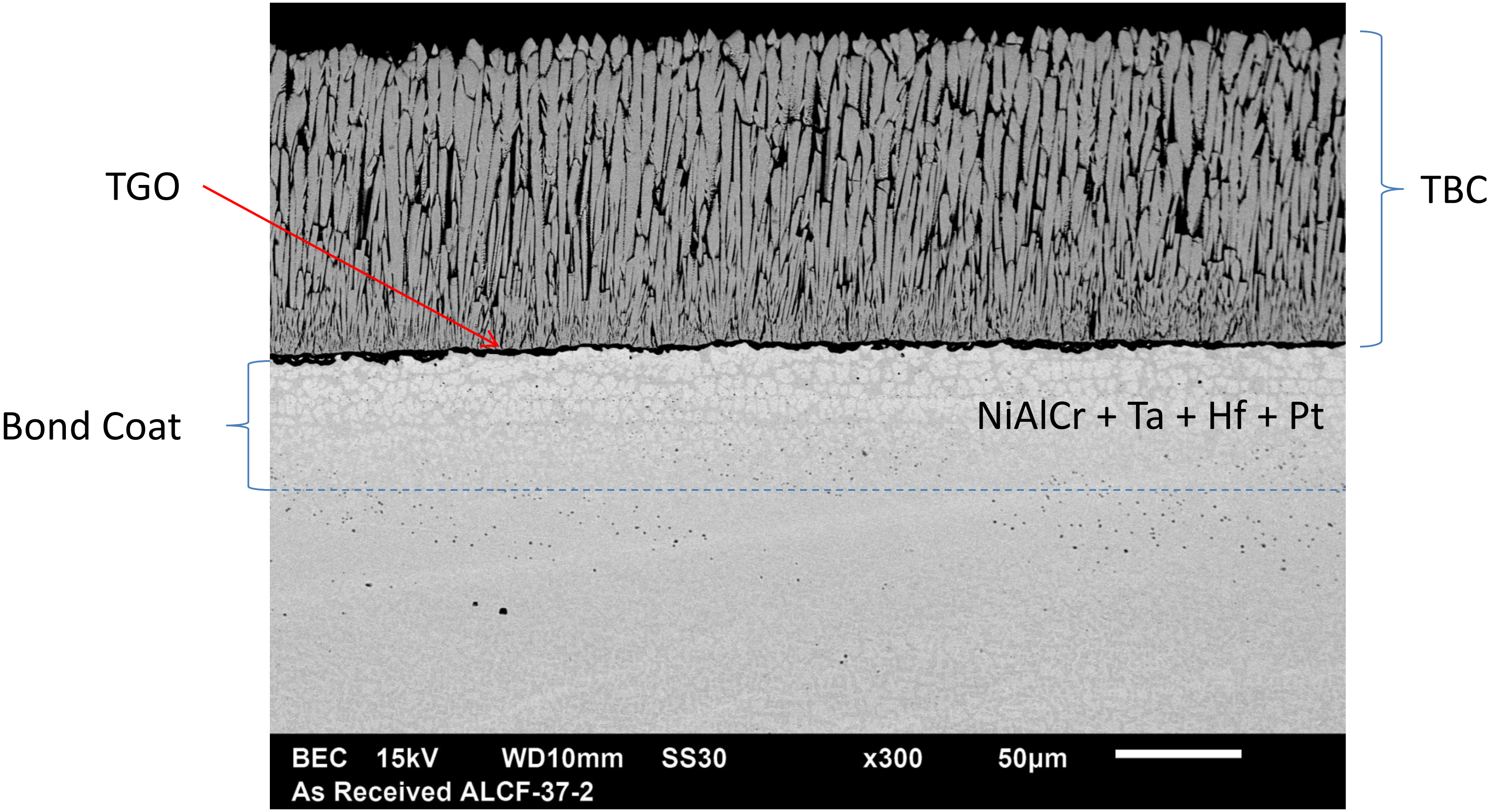


Base Composition: Ni-13Al-7.5Cr-0.1Hf-0.05Y-1Si-0.12C, at.%

• Ta additions to Ni-Al-Cr alloys can beneficially affect the oxide scale formation through partitioning effects including:

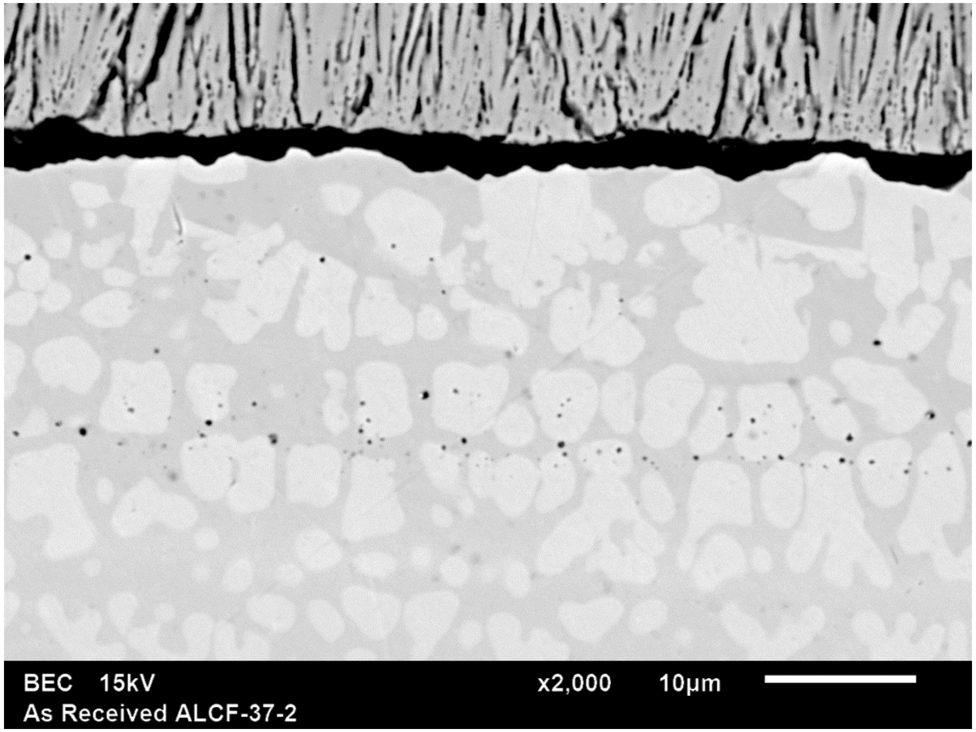
- *Increasing the amount of γ′ phase for a wide temperature range (500-1200 °C).*
- *Increasing Cr in the γ phase and decreasing the Cr in the γ′ phase.*
- *Decreasing Al in both γ and γ′ phases (mass balance holds due to the increasing amount of γ′ phase which has a higher Al concentration).*

Ta Modified Bond Coats



Funded by USAF, Ruth Sikorski

Ta Modified Bond Coats



TBC System lifetime: (1 hr. cycles from 1130^{o}C to room temperature) measured >3000 hours. Additional testing in progress

Background - High Entropy Alloys

- High entropy alloys (HEA) are alloys with five or more principal elements (each having a concentration between 5 and 35 at.%).

- These alloys are designed to have significantly higher mixing entropies than conventional alloys which results in the formation of solid solution phases with simple crystal structures. The high mixing entropy lowers the Gibbs free energy, G, for formation for the solid solution phases ($G = H-TS$) making them more likely to form than the intermetallic compounds which typically result in poor engineering properties.

- HEAs can result in enhanced alloy properties in many areas including excellent high temperature strength, good structural stability, low diffusion coefficients, good creep resistance and good oxidation and corrosion resistance.

- These effects make well designed HEAs excellent candidates for next generation, high temperature structural alloys or as high temperature coatings. *In this work, the use of HEAs as advanced bond coats for thermal barrier coating systems used on gas turbine engine components are considered.*

Compositional Selection

- When considering the development of novel bond coats based on HEAs, consisting of at least 5 major alloying components between 5 and 35 at.%, care must be taken to simplify the compositional degrees of freedom as much as possible based on the engineering requirements of the end solution.

- For example, due to the need for oxidation resistance, alloying elements that promote the formation of a protection oxide scale are clearly required when considering HEAs that could provide further improvements beyond current bond coat systems.

- This requirement constitutes the presence of Al and due to its beneficial effect on the formation of the desired alpha-alumina TGOs, Cr.

- In addition, the levels of Al and Cr required to get good oxidation performance in Ni-based alloys are most widely studied. Thus, if a Ni based composition is used a good estimate of the desired Al and Cr levels can be made.

- ***By choosing a starting Ni-Cr-Al composition, the issue of compositional selection can be simplified to determining the Ni-Al-Cr composition and then choosing alloying elements (at least two) that would substitute for Ni atoms and enable the formation of a HEA alloy***.

Initial Materials of Interest

- Using Ni-Al-Cr (at%) as a base, the selection of alloy elements which may be substituted for Ni is then required.

Element	$T_m(K)$	Atom Size *(pm)*	Electro-negativity	Vapor Pressure *mm-Hg(@2000K)*
Ni	1,728	126	1.91	2×10^{-1}
Al	933	141	1.61	6
Cr	2,180	130	1.66	1
Cu	1,358	126	1.9	3
Co	1,768	124	1.88	2×10^{-1}
Fe	1,811	126	1.83	3×10^{-1}
Ti	1,941	142	1.54	1×10^{-2}
Mn	1,519	132	1.55	1×10^{2}
Mo	2,896	139	2.16	2×10^{-7}
Nd	1,289	182	1.14	---
Nb	2,750	150	1.6	3×10^{-9}
V	2,183	134	1.63	2×10^{-3}
Y	1,795	173	1.22	2×10^{-2}
Si	1,687	112	1.9	3×10^{-2}

Co, Fe, Cu and Mn were considered the baseline additions

- Our approach for selecting these elements would be to identify elements which are not likely to greatly affect the existing phase constitution space when substituted in for Ni based on Hume-Rothery predictions.

SBIR Approach

Phase I: Used quasi-combinatorial technique to experimental assess a range of potential HEA compositions

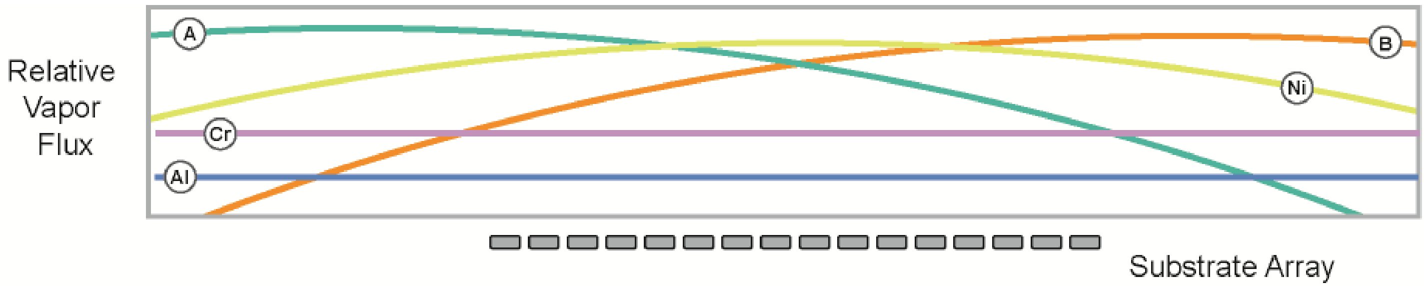
	Co	Fe	Cu	Mn
Co	~~Co-Co~~	~~Co-Fe~~	~~Co-Cu~~	~~Co-Mn~~
Fe	Fe-Co	~~Fe-Fe~~	~~Fe-Cu~~	~~Fe-Mn~~
Cu	Cu-Co	Cu-Fe	~~Cu-Cu~~	~~Cu-Mn~~
Mn	Mn-Co	Mn-Fe	Mn-Cu	~~Mn-Mn~~

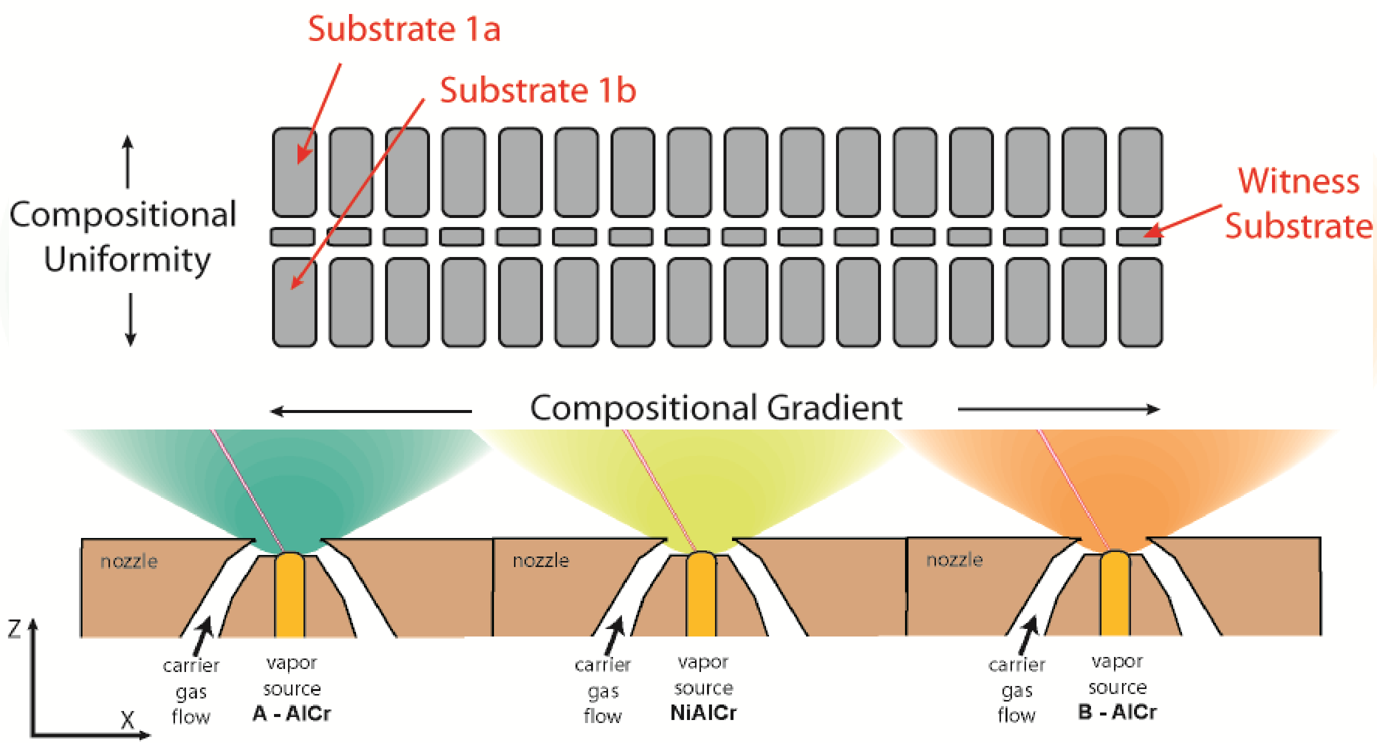
Phase II: Use both experimental and computational techniques to optimize HEA compositions of interest

Experimental: quasi-combinatorial assessment and full bond coat application

Computational: HEA system prediction and chemical activity matching

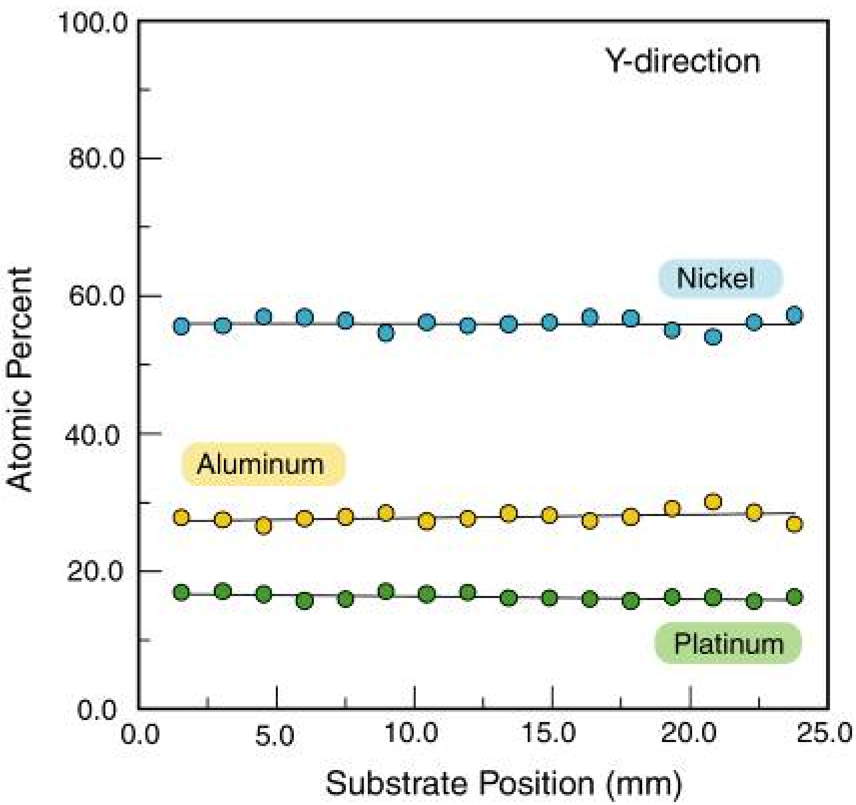
Quasi- Combinatorial Synthesis



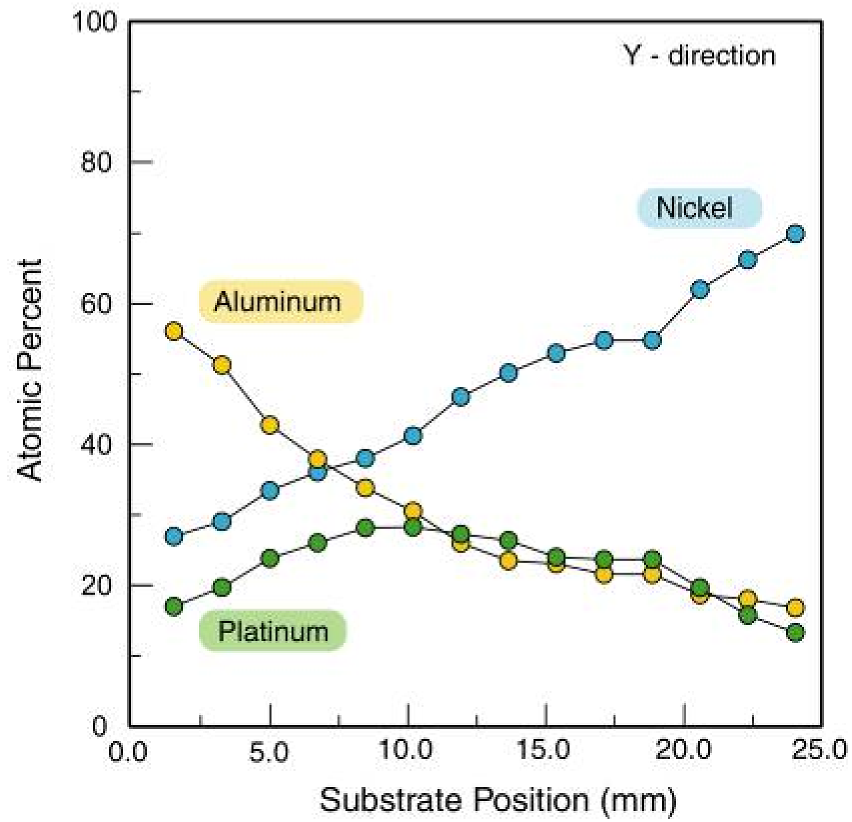


Multi-source Deposition

Moderate Chamber Pressure (0.10 Torr)

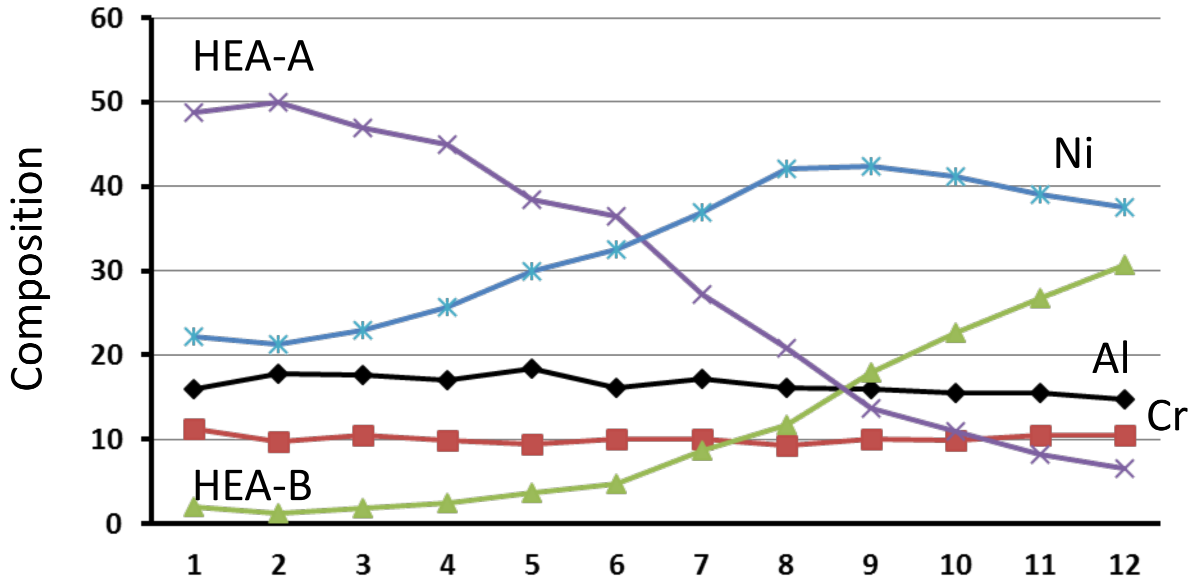


High Chamber Pressure (0.44 Torr)



Quasi- Combinatorial Synthesis

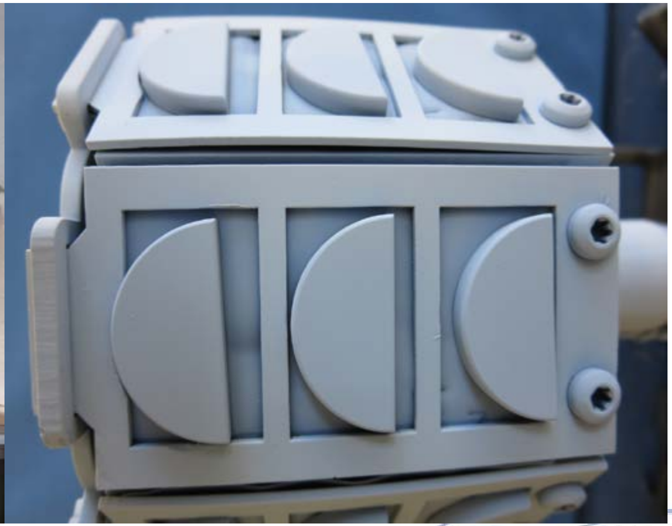
Compositional Gradient Achieved



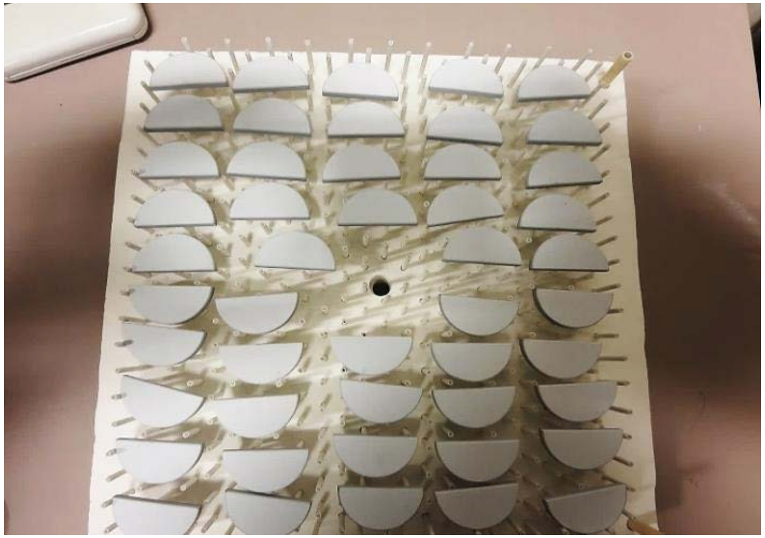
Quasi- Combinatorial Synthesis

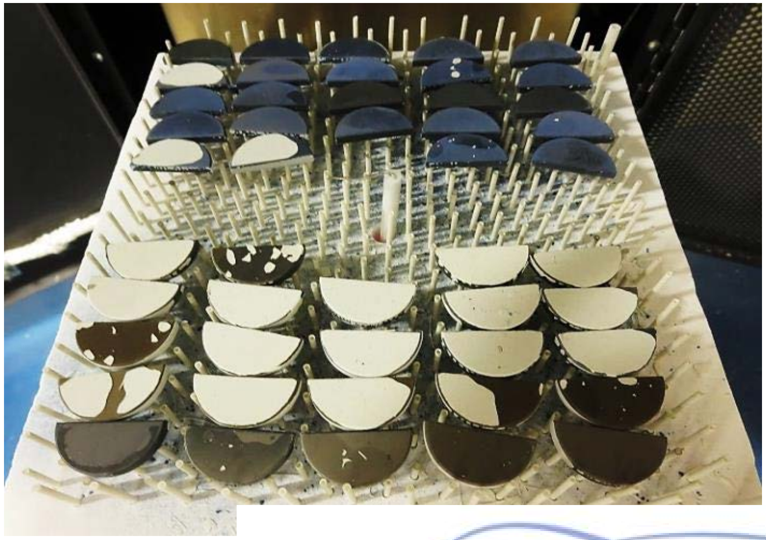
Top Coat Application

7YSZ Top Coats applied onto each set of HEA bond coat compositions



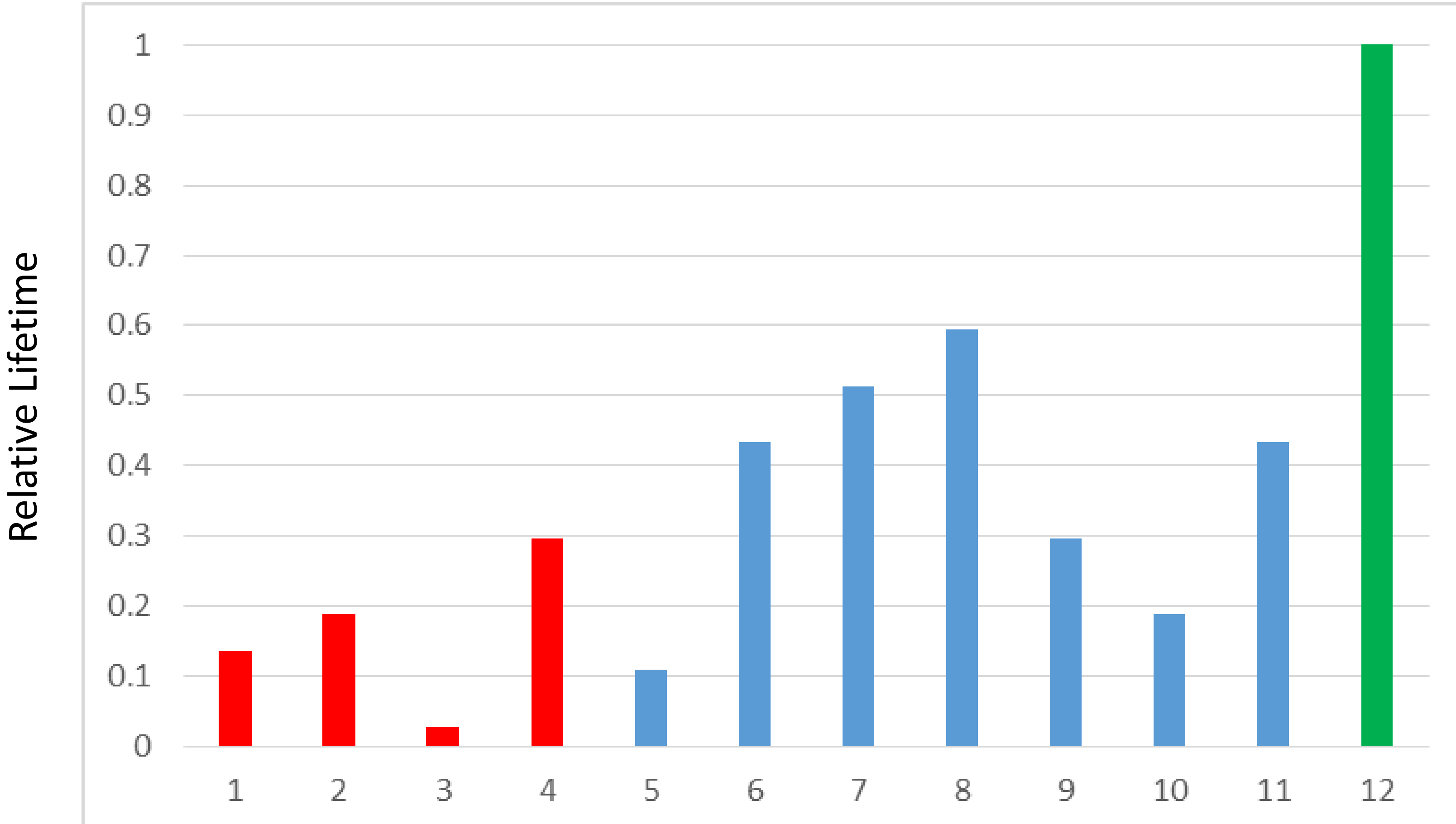
Thermal Spallation Testing





Thermal Spallation Testing

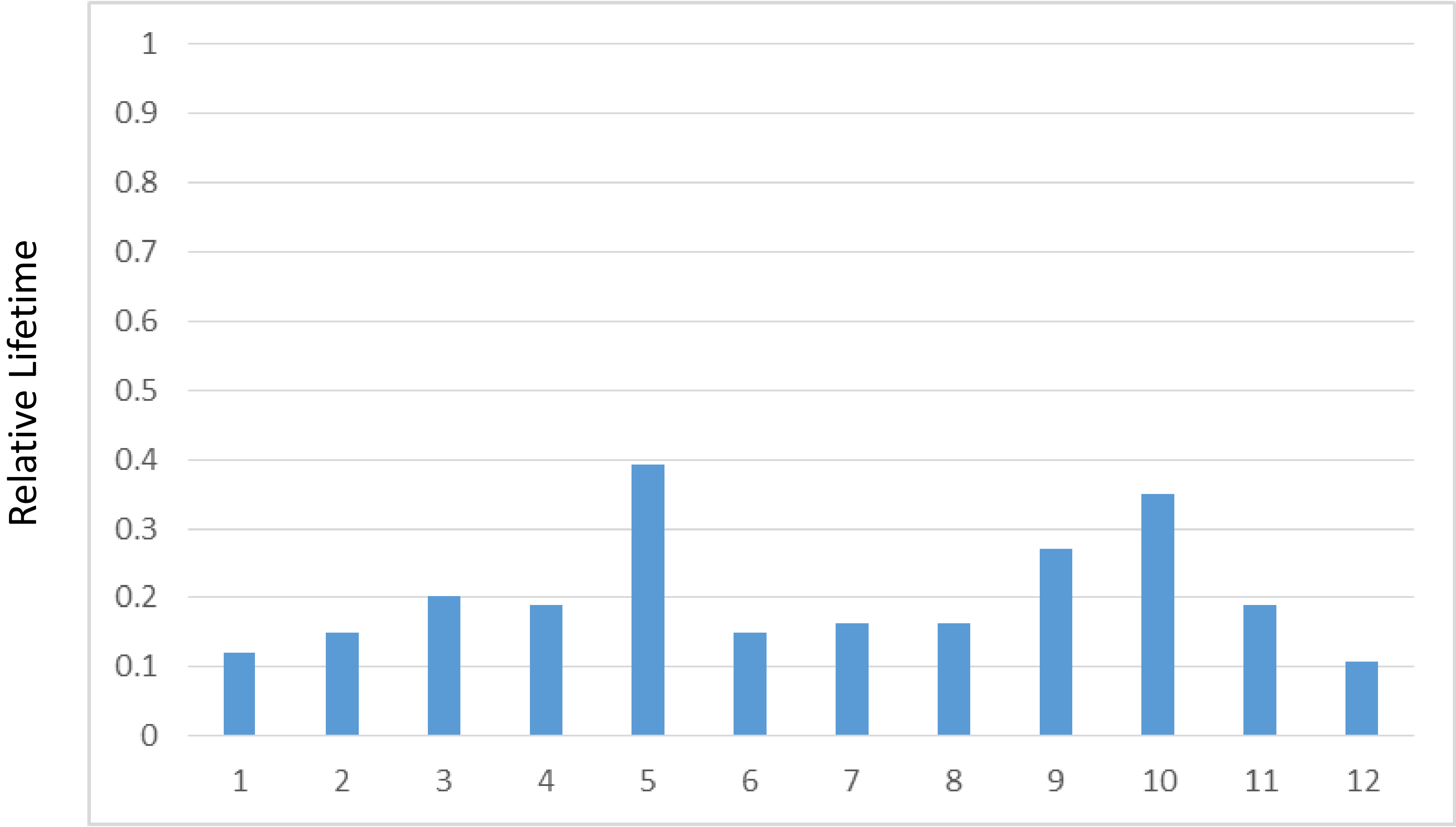
NiCuFeAlCr



Green indicates compositions that fit the description of HEA alloys and also have promising cyclic oxidation lifetimes. Red indicates the composition does not fit the description of an HEA alloy.

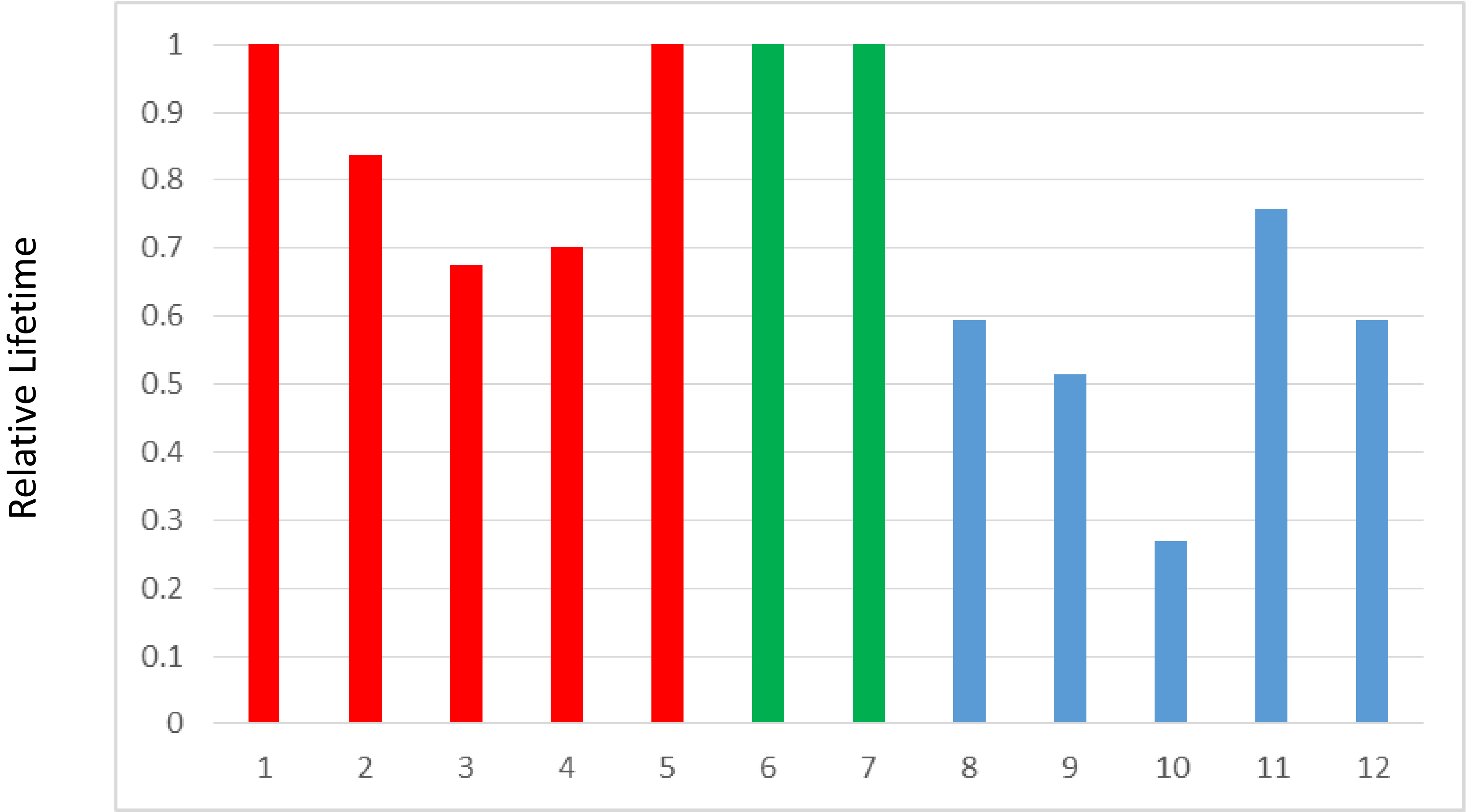
Thermal Spallation Testing

NiCuCoAlCr



Thermal Spallation Testing

NiCoFeAlCr



Surface Microstructure

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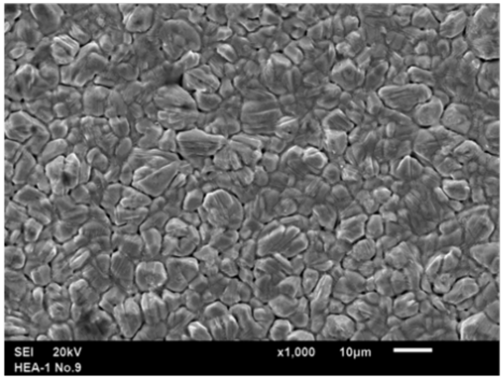

* Sample 9 was misplaced.

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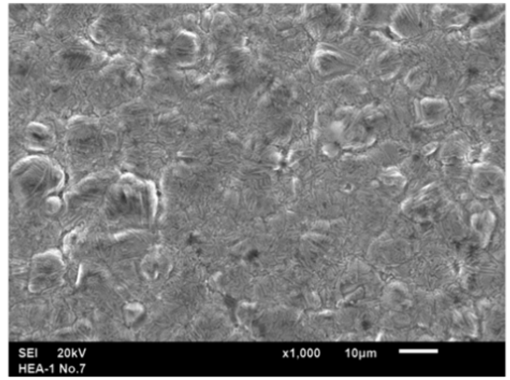

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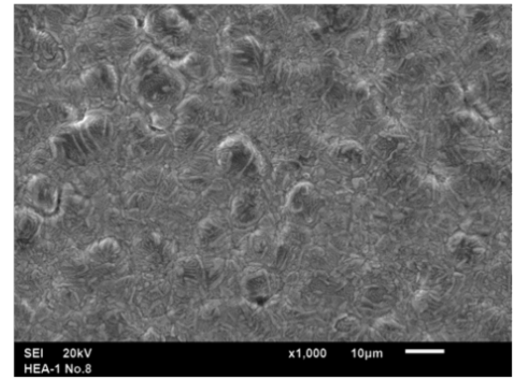

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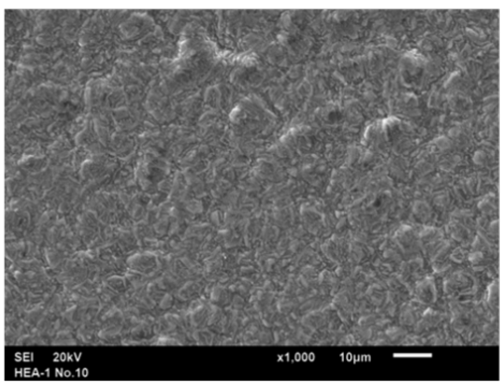

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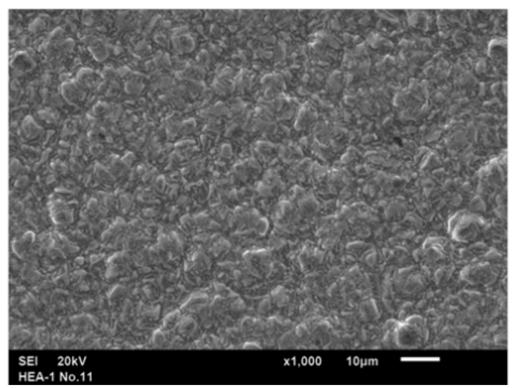

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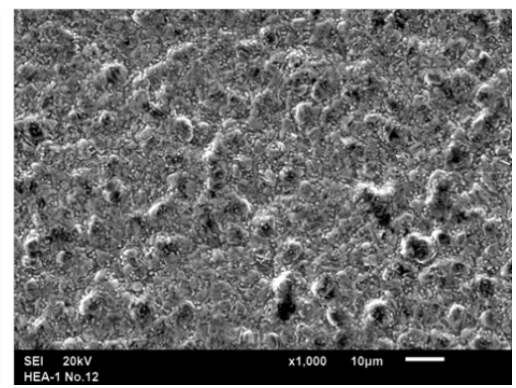
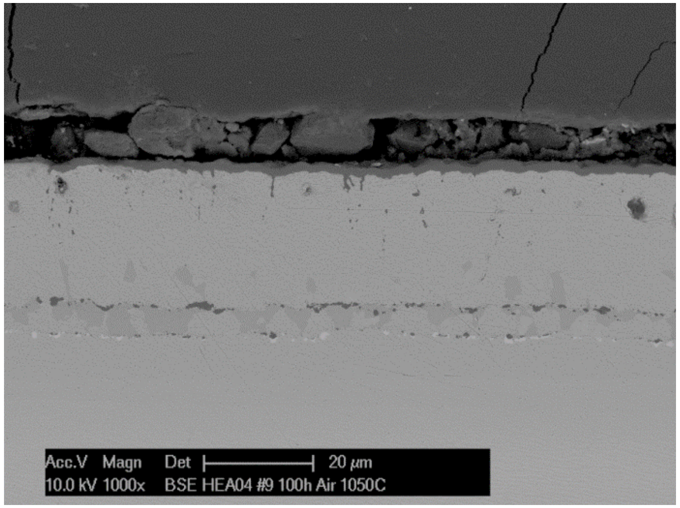


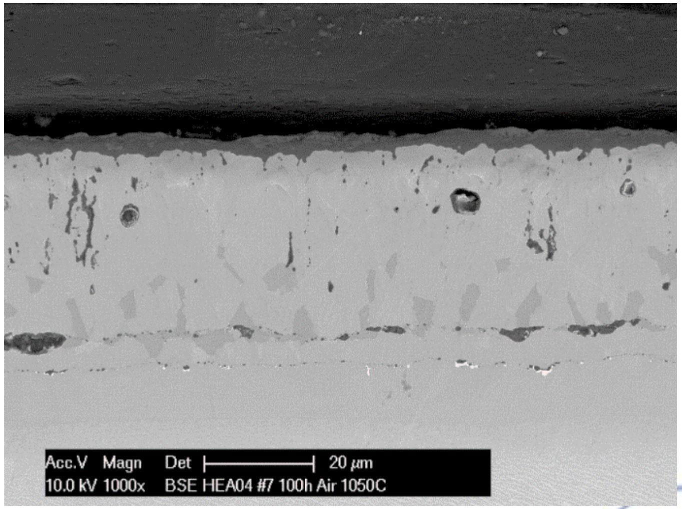
Oxidation Testing

- The results indicated that a well adhered alpha alumina scale was formed on all samples. As this is a critical component to any good performing TBC system, this was an encouraging result.
- No TCP phase formation due to substrate / coating interaction
- The coating microstructure was generally dense, however, some columnar porosity resulting in selected compositions. This resulted in some internal oxidation. This feature can likely be eliminated by slight alternations to the plasma activation conditions used and therefore is not a concern at this stage.

HEA-4 #9



HEA-4 #7



100 hours at 1050°C in air

TBC Systems with HEA Bond Coats

Optimization of TBC system performance using identified HEA bond coat compositions through the incorporation of minor alloy element additions to optimize oxidation performance and densification of the coating microstructure through modification of the plasma activation parameters.

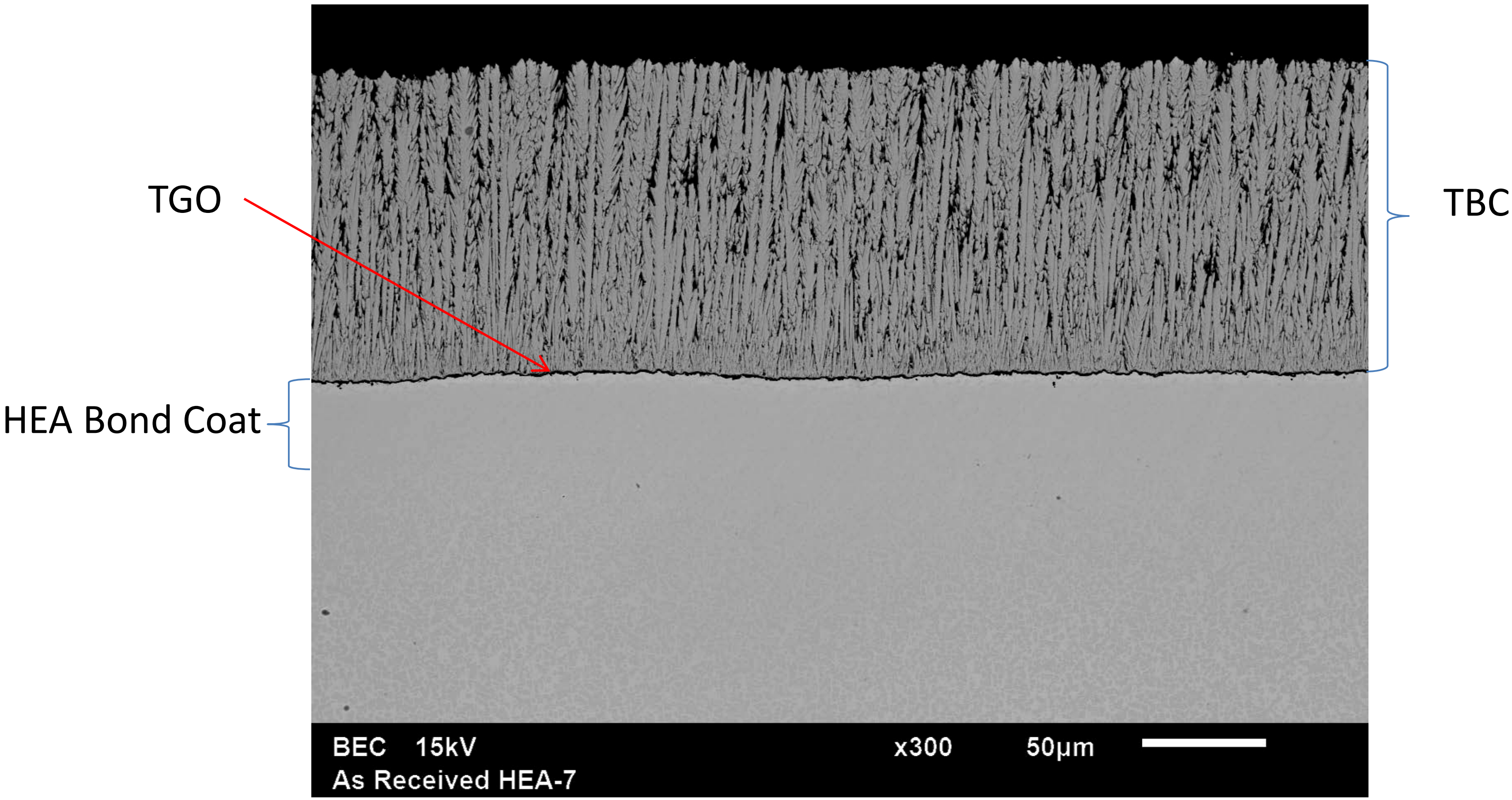
Two bond coat compositions were identified during the Phase I effort that showed promising performance in thermal spallation and oxidation testing

System A: NiCuFe-20Al-5Cr.

System B: NiCoFe-17Al-10Cr

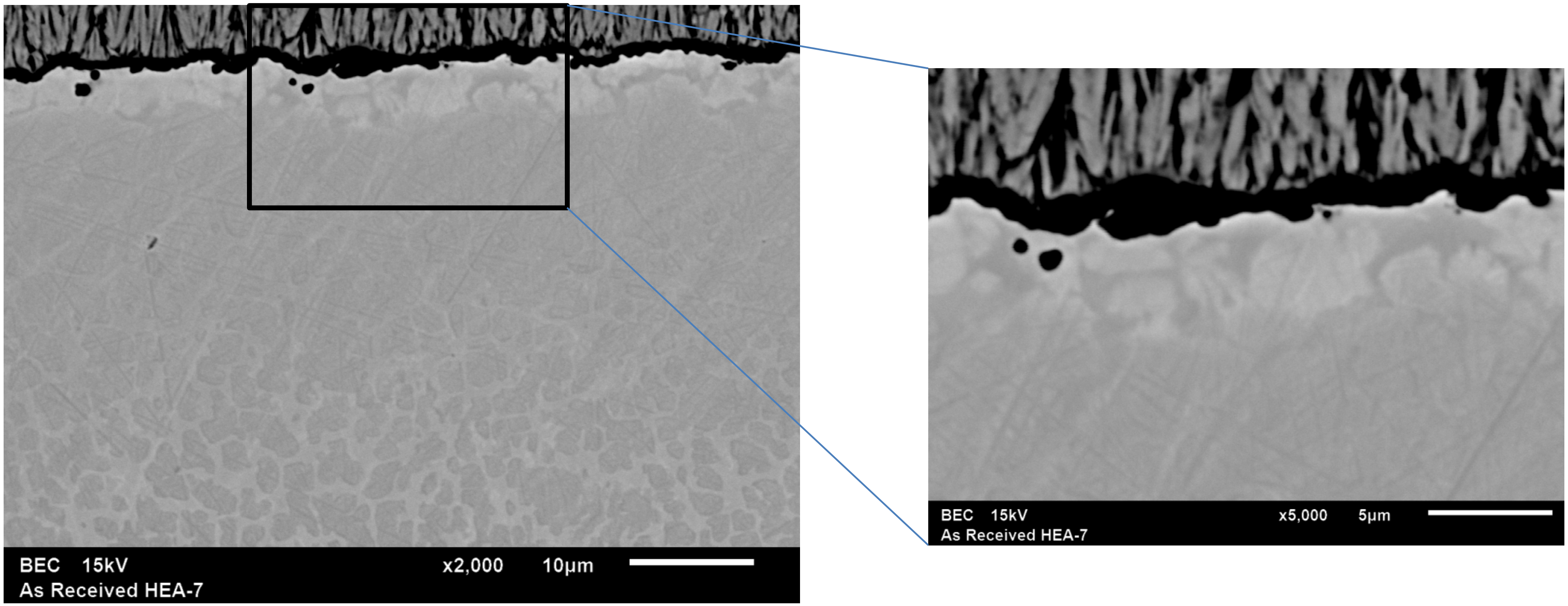
TBC Systems with HEA Bond Coats

System A: NiCuFe-20Al-5Cr + Hf + Pt



TBC Systems with HEA Bond Coats

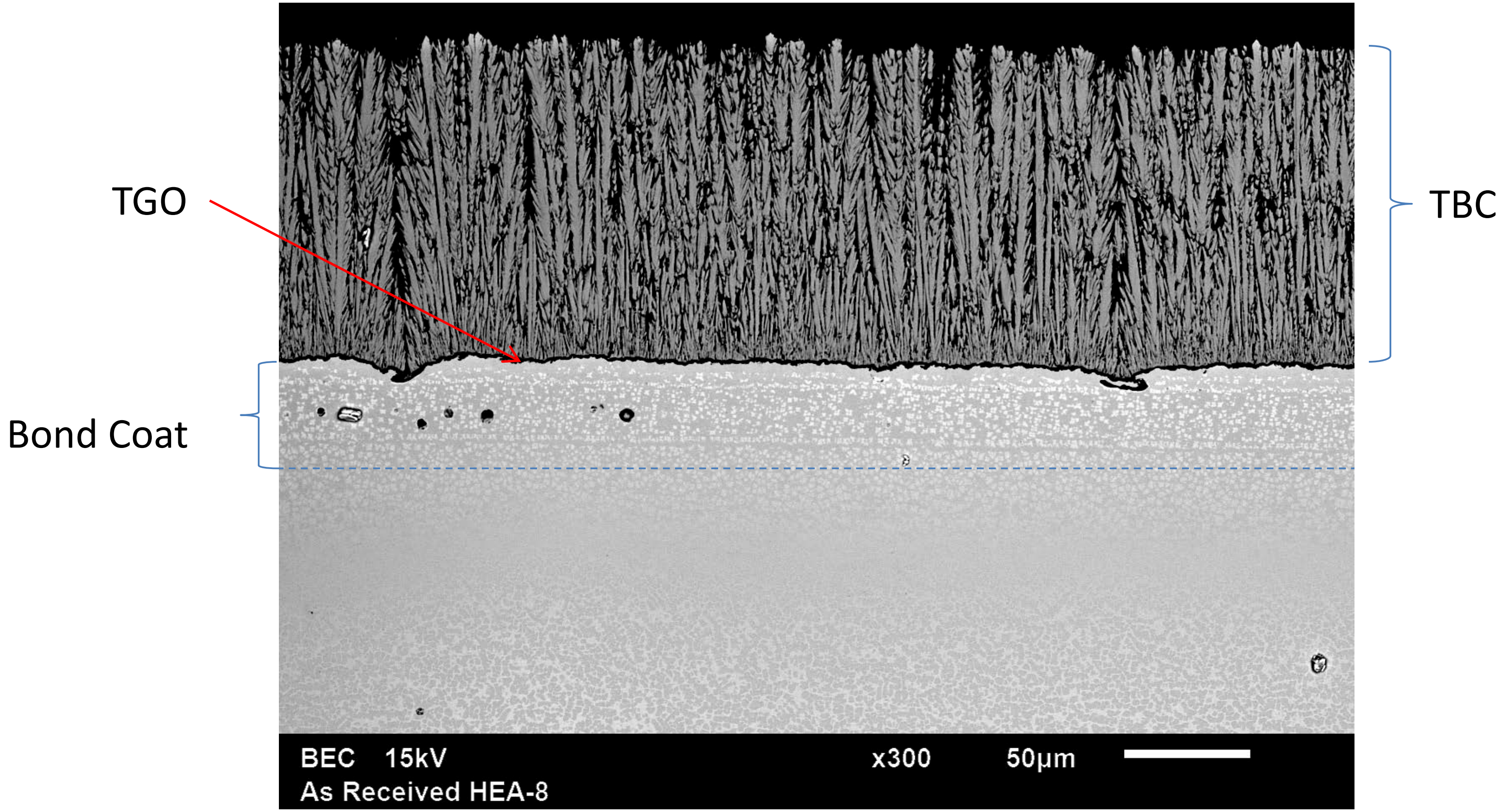
System A: NiCuFe-20Al-5Cr + Hf + Pt



XRD indicates crystalline bond coat with multiple phases present. Further analysis in progress

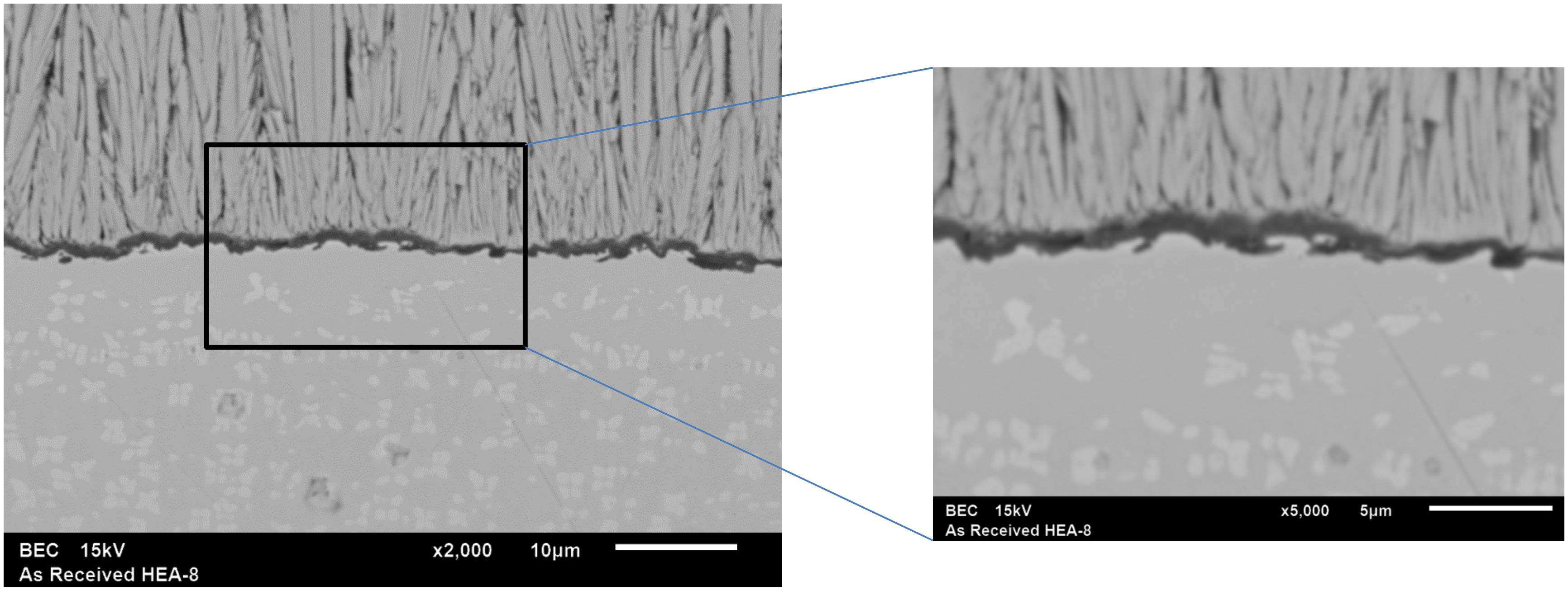
TBC Systems with HEA Bond Coats

System B: NiCoFe-17Al-10Cr



TBC Systems with HEA Bond Coats

System B: NiCoFe-17Al-10Cr



- Appears to be two-phase
- XRD analysis in progress

TBC Systems with HEA Bond Coats

TBC System lifetimes: 1 hr. cycles from 1130^{o}C to room temperature)

Coating Type	Cycles	Failure
HEA System A	576	Yes
HEA System A	744	Yes
HEA System A	216	Yes
HEA System B	> 984	No
HEA System B	> 984	No
HEA System B	648	Yes
Baseline	~700	Yes

HEA System B shows good TBC lifetimes in initial cyclic oxidation testing

CalPHAD for HEA Development

Use a CalPHAD approach to aid in the design of HEA coating compositions that are compatible with the base Ni-base superalloy owing to chemical activity matching.

This approach can be used to predict both:

1) HEA alloy formation
2) The activity of key elements in multi-component alloys

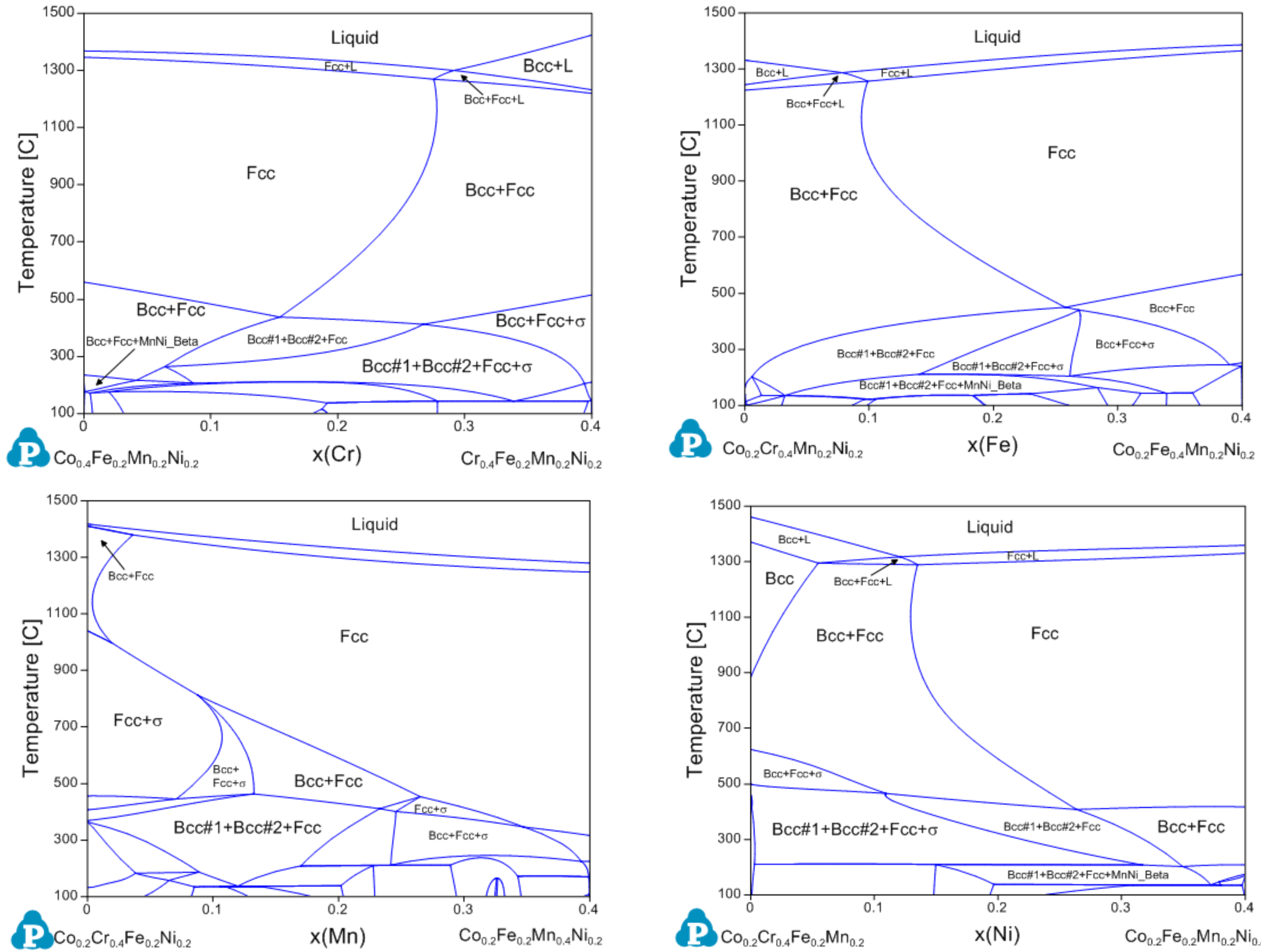
PANDAT™ SOFTWARE

CompuTherm, LLC

437 S. Yellowstone Drive, Madison, WI, USA

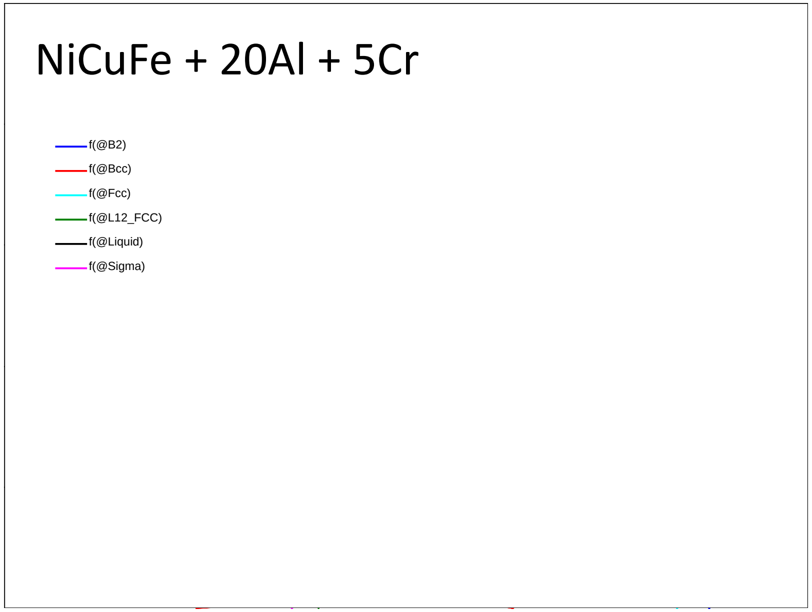
http://www.computherm.com

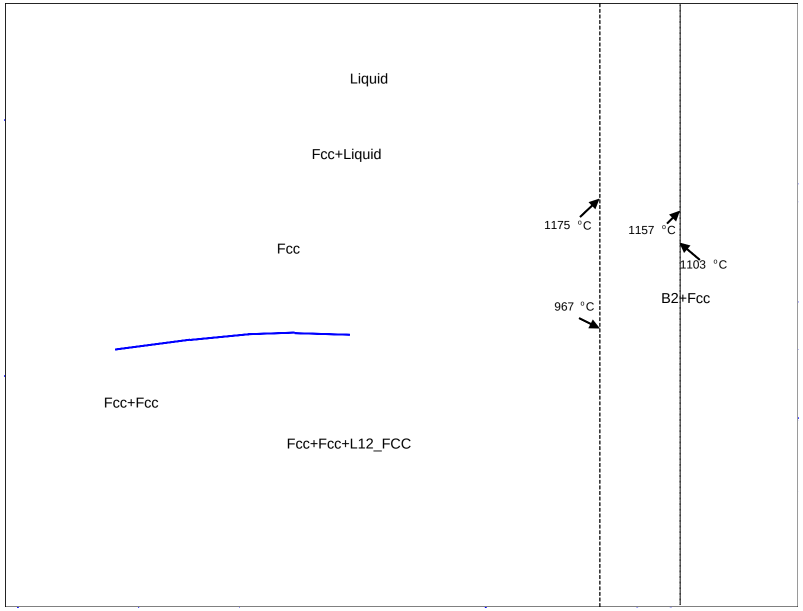
Cr-Mn-Co-Fe-Ni Isopleth Sections



Isopleths calculated for the Cr-Mn-Co-Fe-Ni system. It is seen, FCC is stable in wide composition and temperature. This is why single fcc HEAs were developed in this 5-component system

HEA Bond Coats - CalPHAD



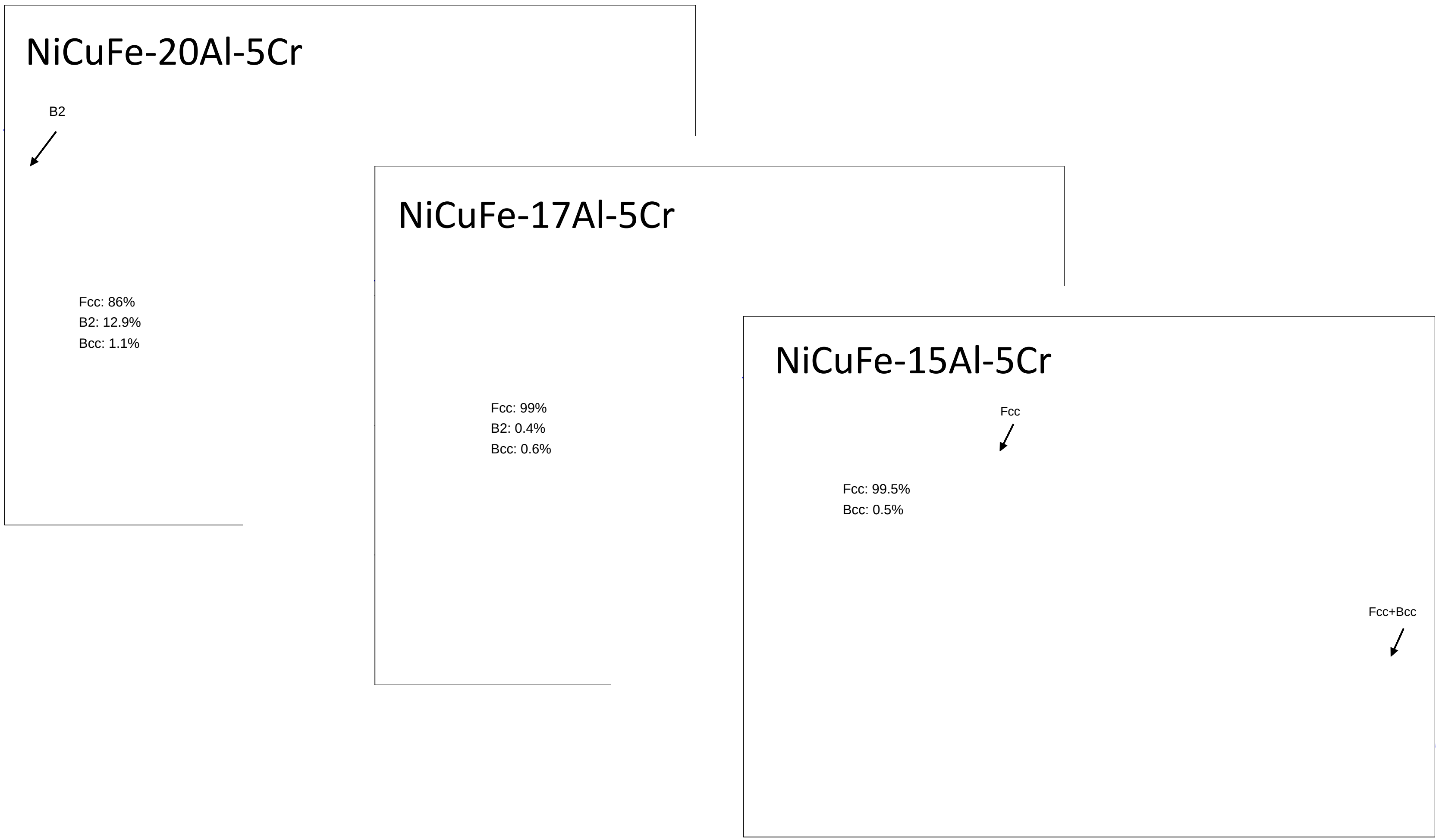


A line calculation was performed for System A NiCuFe + 20Al + 5Cr (at%) alloy at varying temperature from 500°C to 1300°C.

Fcc and B2 form at high temperature, Bcc is stable in the middle temperature, and L12 and Sigma form at low temperature. A temperature range with single solid solution does not exist;

Therefore it is unlikely to develop a single solid solution high entropy alloy (HEA) with this alloy composition under equilibrium condition.

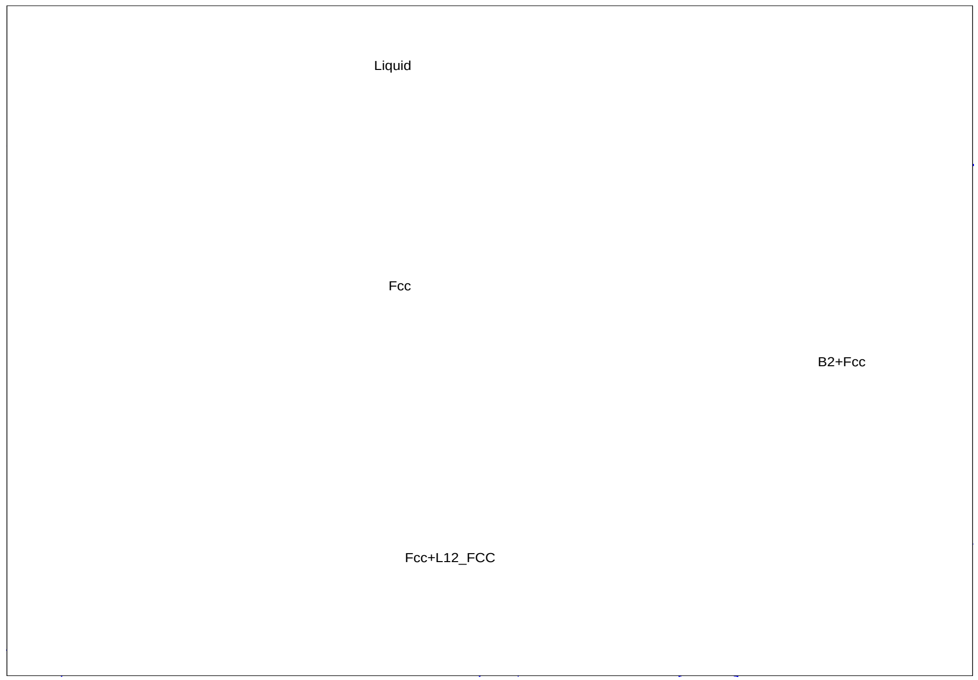
HEA Bond Coats



Solidification simulation for the NiCuFe-xAl-5Cr (at%) alloy using Scheil model

HEA Bond Coats

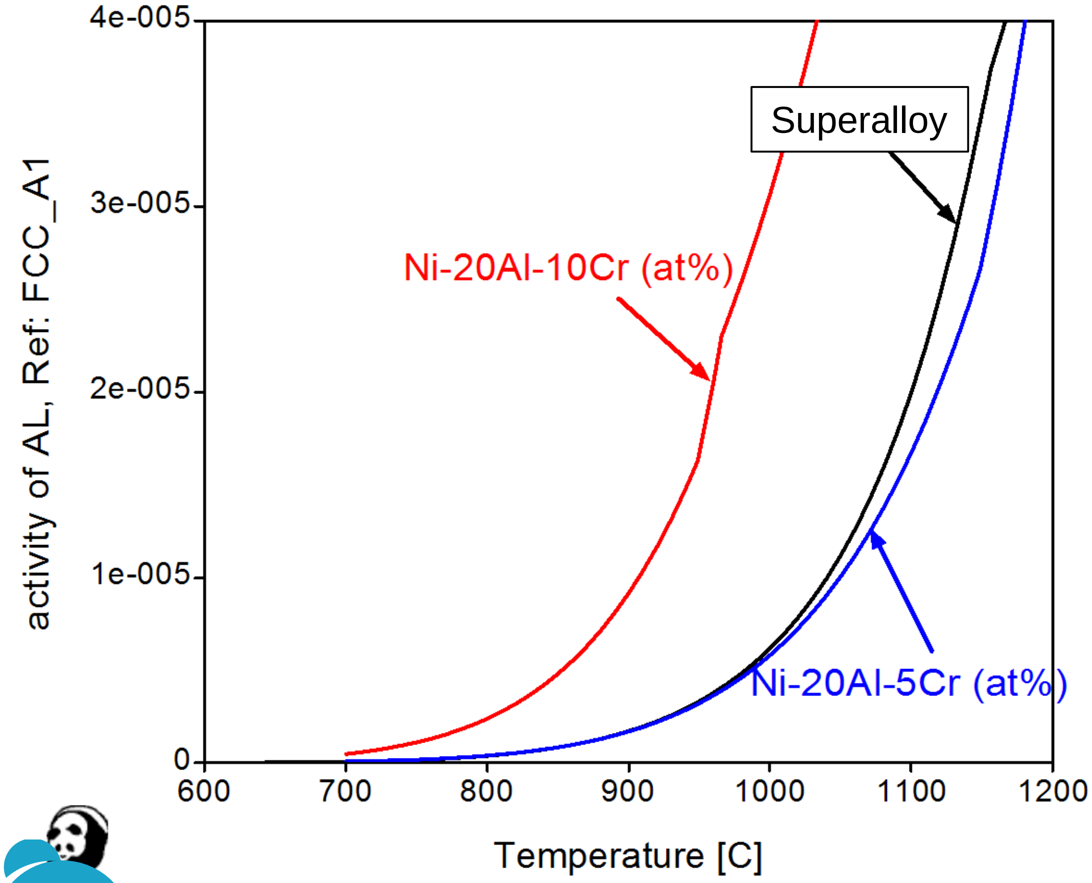
System 2: NiCoFe-xAl-10Cr



FCC is stable in wide composition and temperature range. Good potential for HEA formation if Al content reduced.

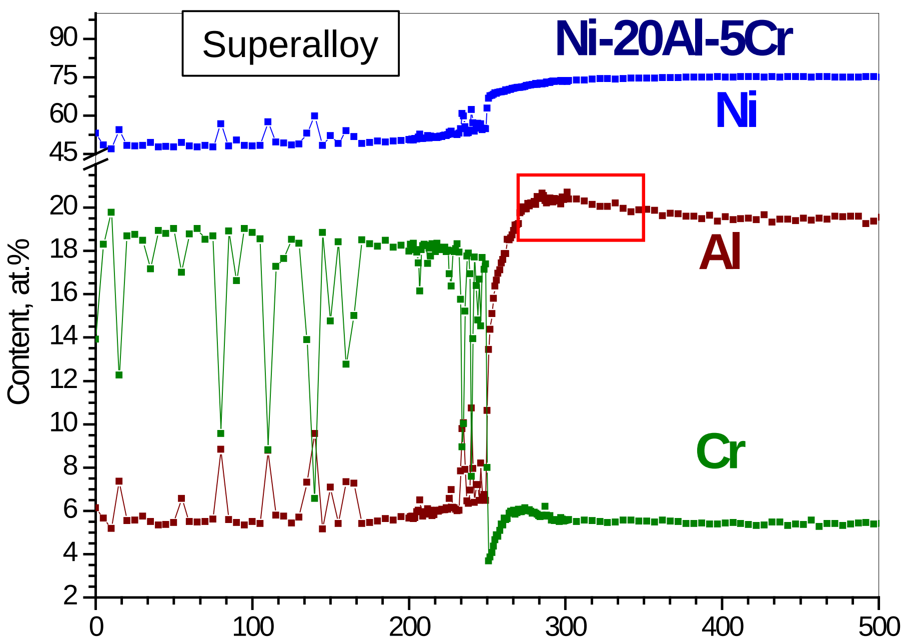
Chemical Activity Matching

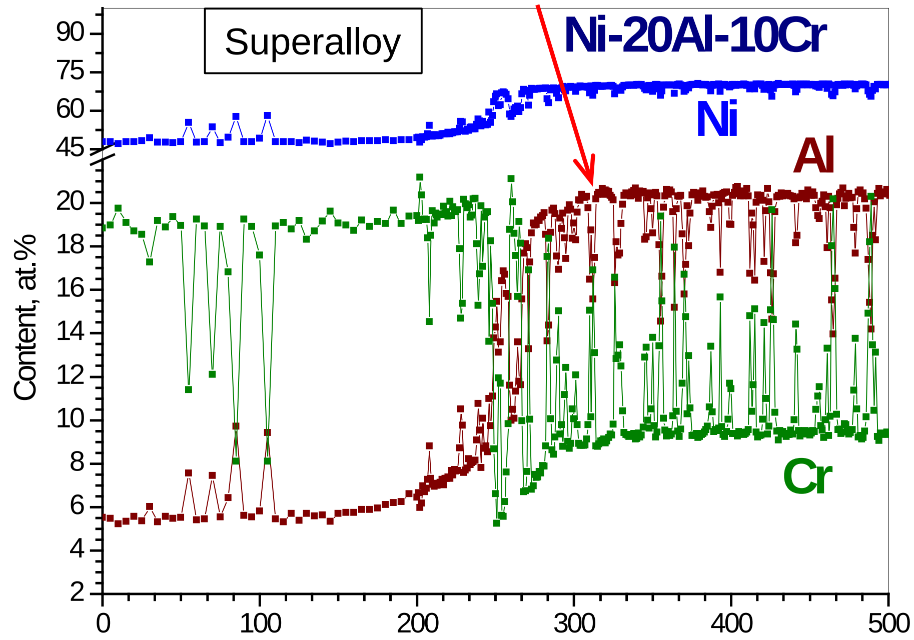
Activity Matching: Minimize Inter-diffusion

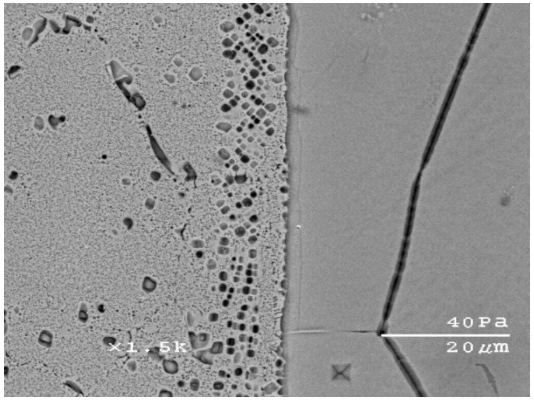


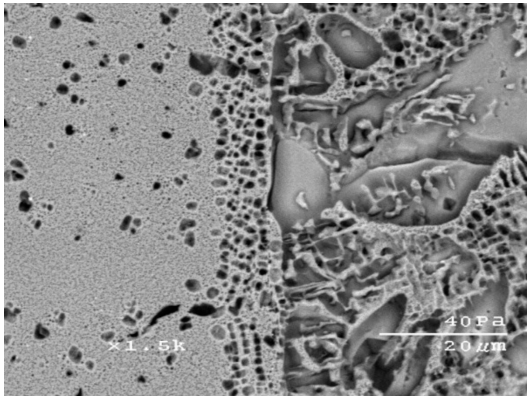
Chemical Activity Matching

Diffusion Couple of Superalloy / Ni-20Al-XCr (annealing at 1100°C for 50hrs)

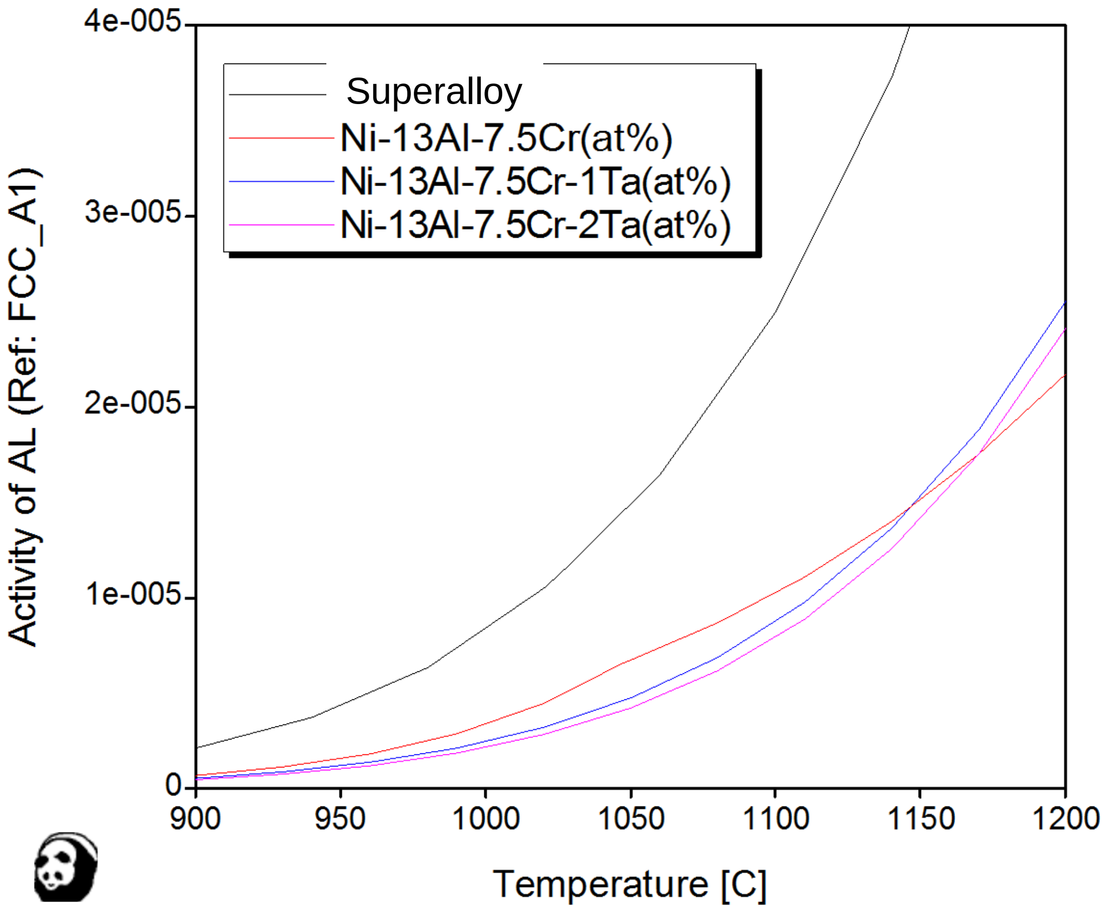








Chemical Activity Matching

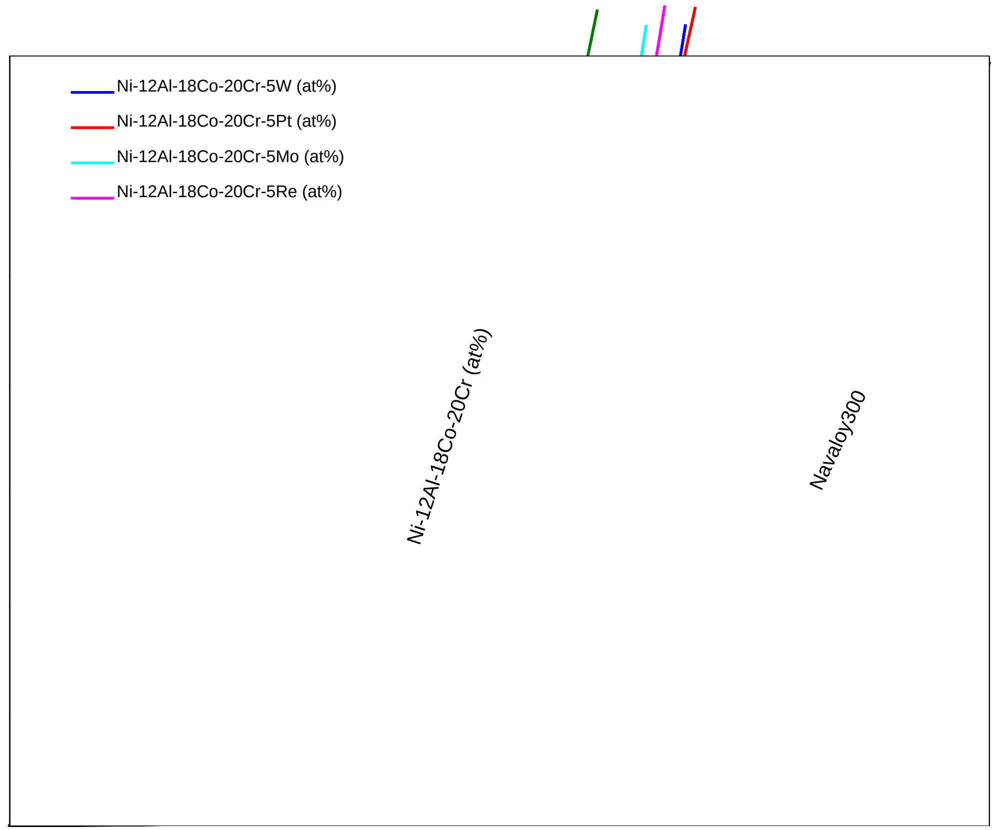


Very low Al activity coatings

- Initial computations indicate that Co, Fe increase Al activity for systems of this type.
- Need to balance with Al activity reducers.

CompuTherm FOR MATERIALS DESIGN

Chemical Activity Matching



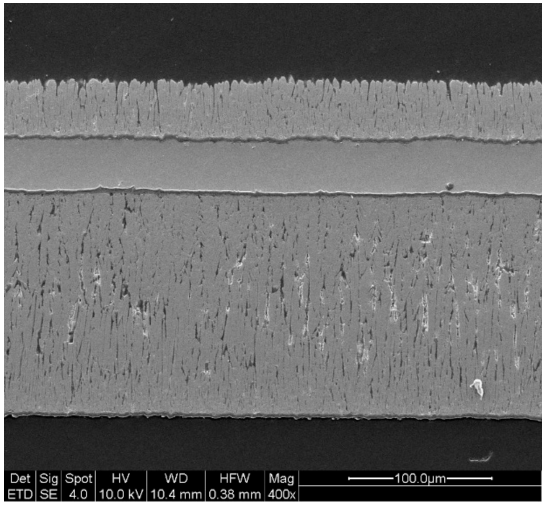
Effects of W, Pt, Mo, and Re on the activity of Al based on a Ni-12Al-18Co-20Cr (at%) alloy

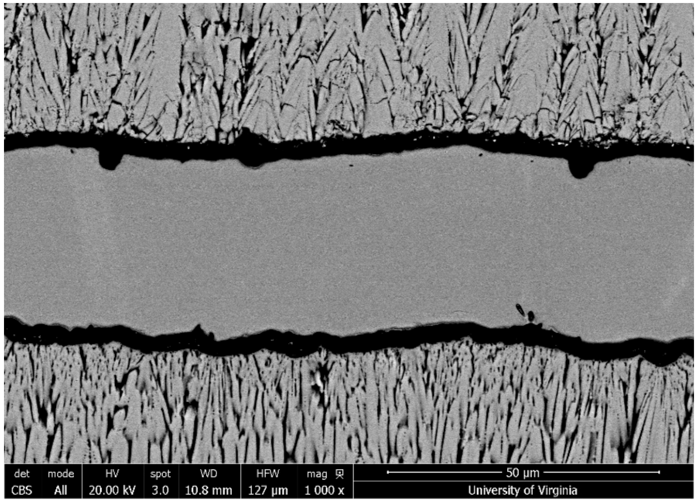
CompuTherm FOR MATERIALS DESIGN

Directed Vapor Technologies International, Inc.

Embedded Interlayers

- Dense interlayers can prevent molten sand / salt infiltration
- Require improved high temperature performance, CTE modification





- YSZ top coat having a NiAlCr coating embedded into the 7YSZ structure following thermal cycling.
- A very dense, well adhered embedded layer is shown that forms a protective TGO layer (the bottom TGO is likely due to edge effects on the coupon sample).
- The TBC system had a similar lifetime with and without the embedded layer.

Next Steps

Use computational and experimental techniques to design HEA bond coats that form FCC or FCC/BCC structures having elevated melting temperatures, good chemical activity matching and enhanced high temperature mechanical properties.

A) Continue combinatorial assessment based on CalPHAD predictions and chemical activity matching studies to identification of additional elements for incorporation.

B) Optimization of TBC system performance using identified HEA bond coat compositions through the **incorporation of minor alloy element additions** to optimize oxidation performance.

C) Assessment of the phases present of the identified HEA compositions using **X-ray diffraction** techniques and CALPHAD predictions.

D) Assessment of the **high temperature properties of the identified high entropy alloys** such as creep strength and high temperature mechanical strength

Summary

- A “quasi” – combinatorial (QC) technique has been developed and used to assess multiple potential HEA bond coat compositions.

- Demonstrated the ability to obtain suitable lateral compositional gradient across a substrate array using the QC set-up. This was confirmed using surface EDS measurements of as-deposited arrays of HEA compositions.

- Candidate compositions have been incorporated into TBC systems and have demonstrated suitable TBC lifetimes.

- Computational techniques and being used to identify additional elements for experimental study. Elevated melting points and good chemical activity matching are sought.

- Assessment of TBC system performance and high temperature mechanical properties will be utilized to demonstrate potential performance benefits.