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

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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

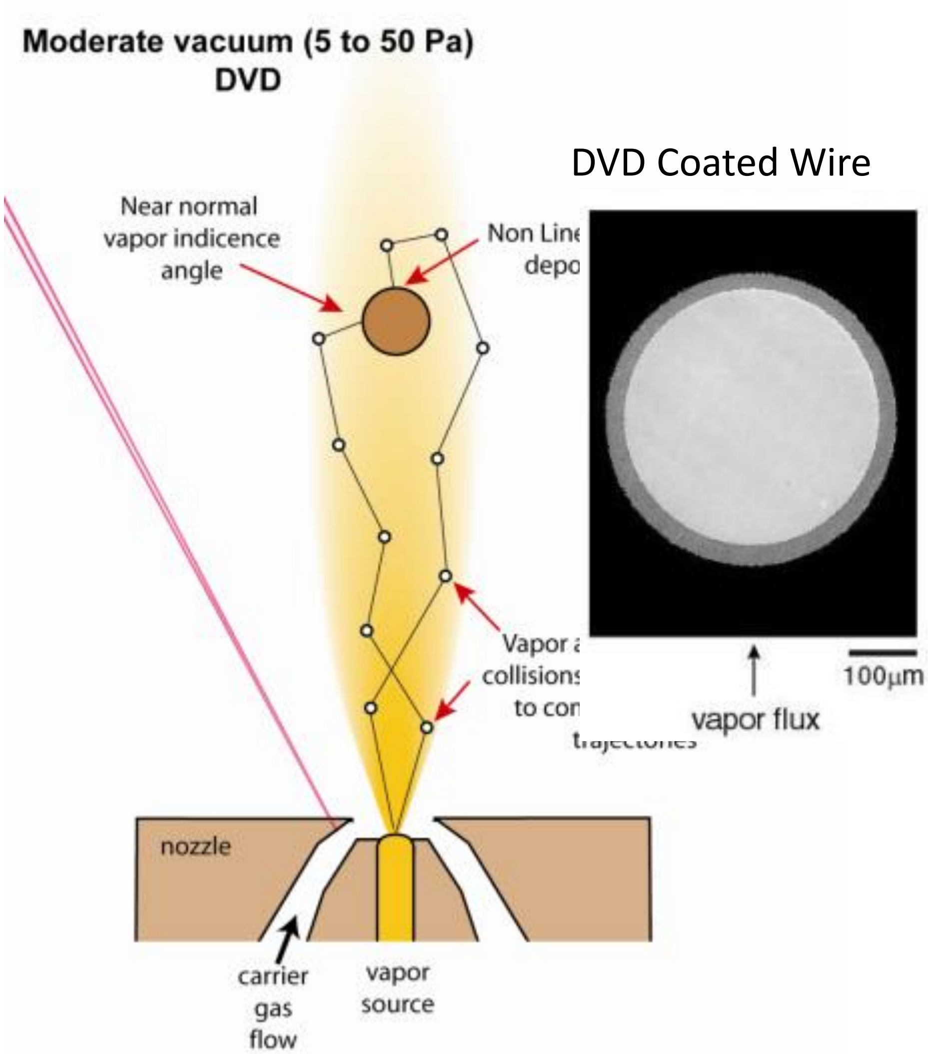
Directed Vapor Deposition

Concept

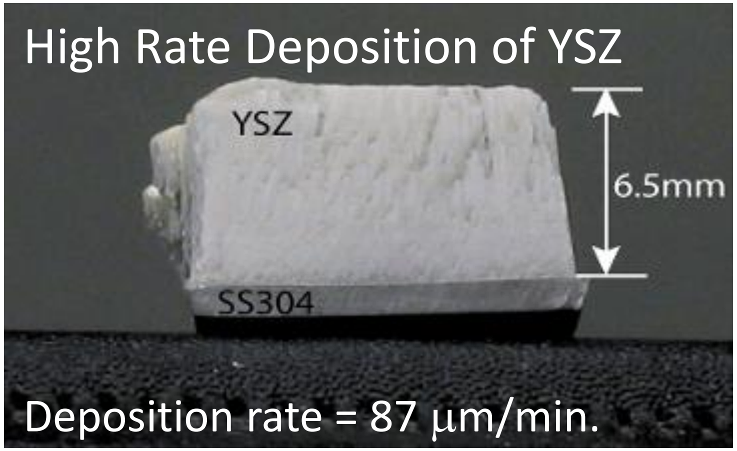
gas phase scattering of an evaporated vapor flux (by collisions with supersonic gas) enables the flux trajectory to be controlled

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



High Rate Deposition of YSZ



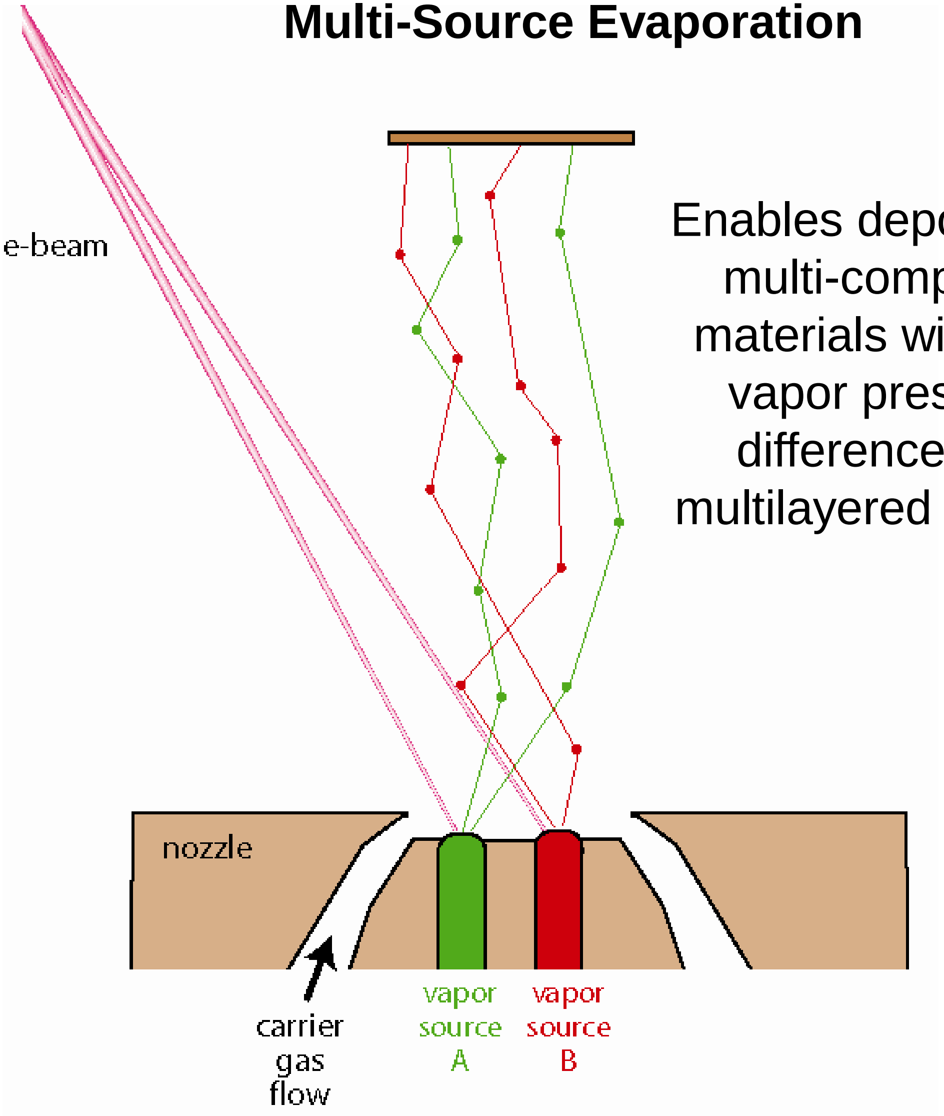
Deposition rate = 87 µm/min.

DVD Advantages:

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

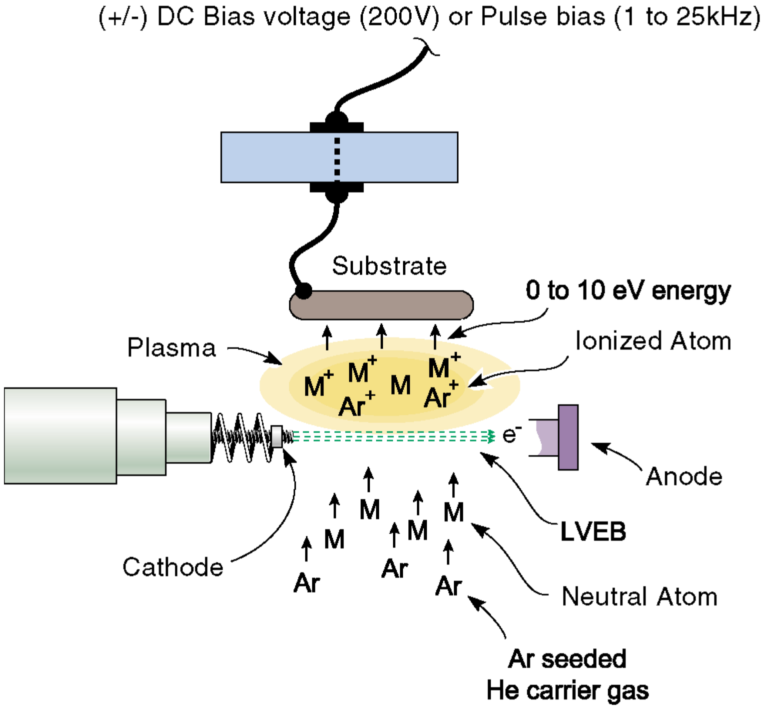
Directed Vapor Deposition

Multi-Source Evaporation

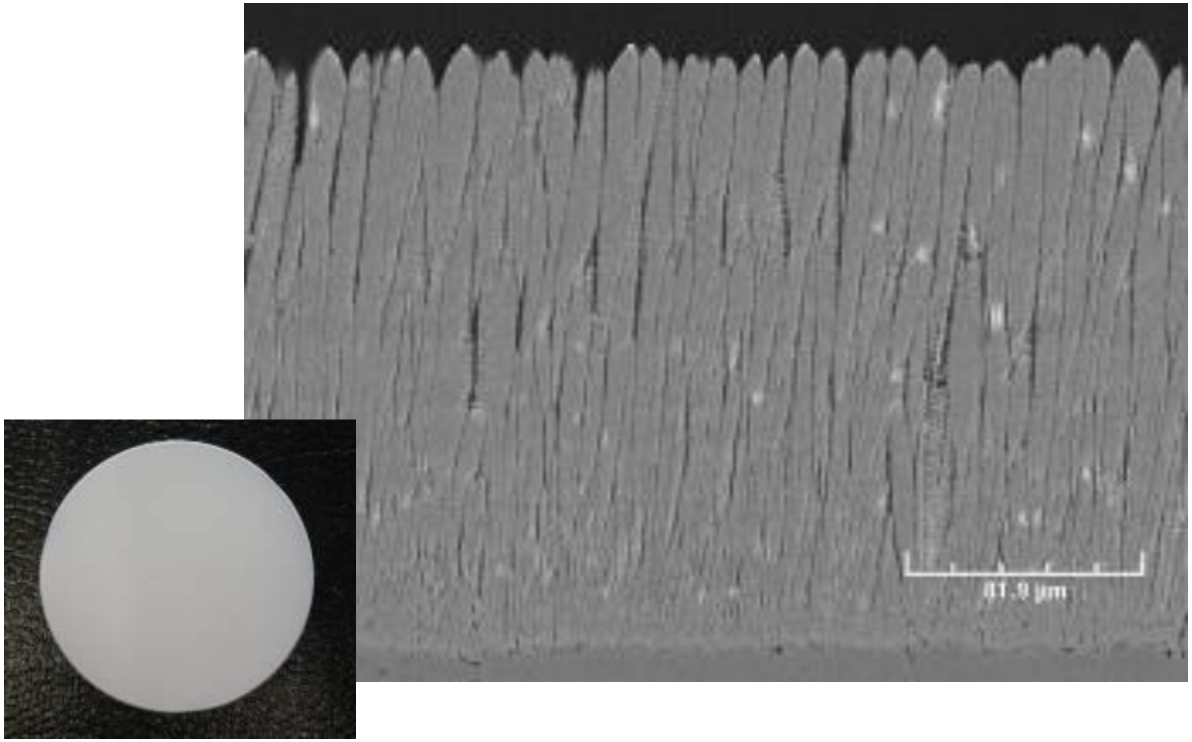


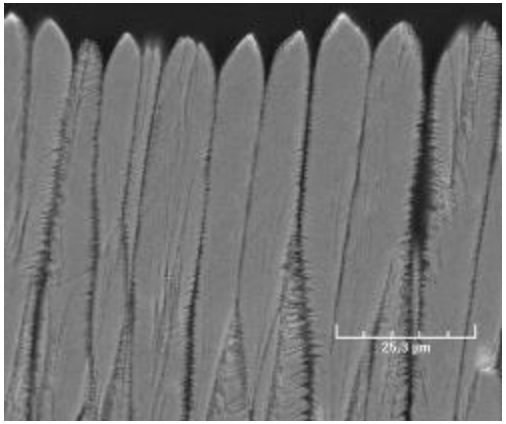
Enables deposition of multi-component materials with large vapor pressures differences and multilayered coatings

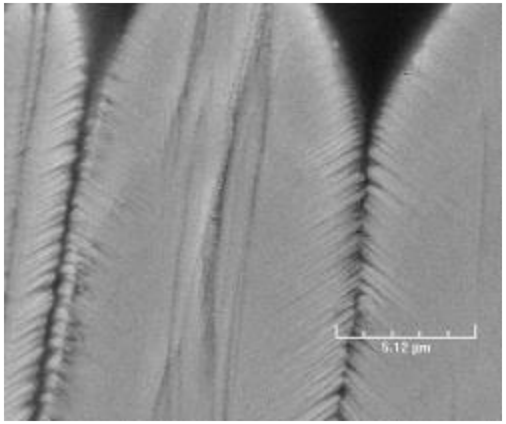
DVD with Plasma Activation



TBC Top Coats







Cyclic Oxidation

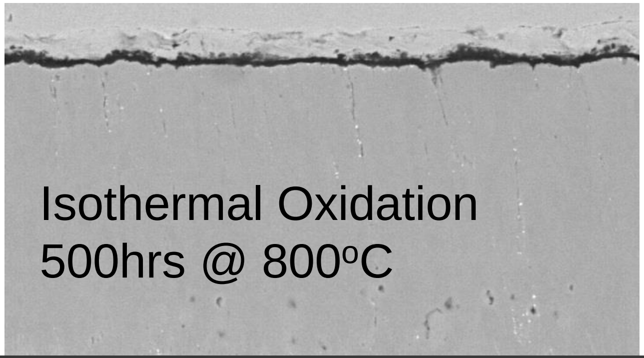
Coating Type	Cycles to Failure
EB-PVD 7 YSZ / CVD PtAl / CMSX-4	1.0X
EB-DVD 7 YSZ / CVD PtAl / CMSX-4	1.5X

1 hr cycles @ 1120°C

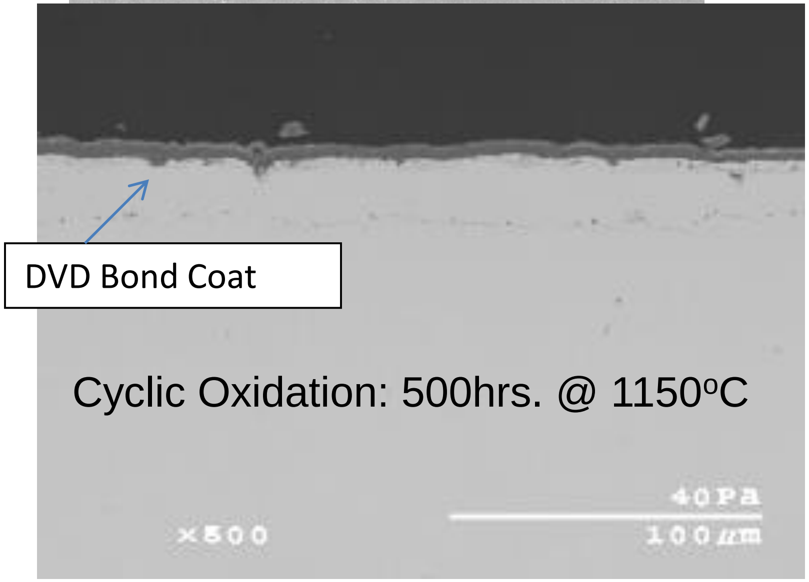
Oxidation and Hot Corrosion Resistance

High Temperature Oxidation

Modified NiAl alloys



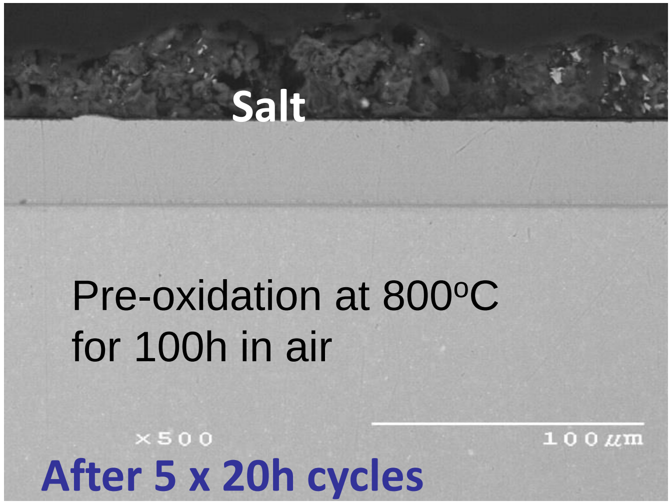
Isothermal Oxidation
500hrs @ 800°C



DVD Bond Coat

Cyclic Oxidation: 500hrs. @ 1150°C

Hot Corrosion Resistance



Pre-oxidation at 800°C
for 100h in air

After 5 x 20h cycles

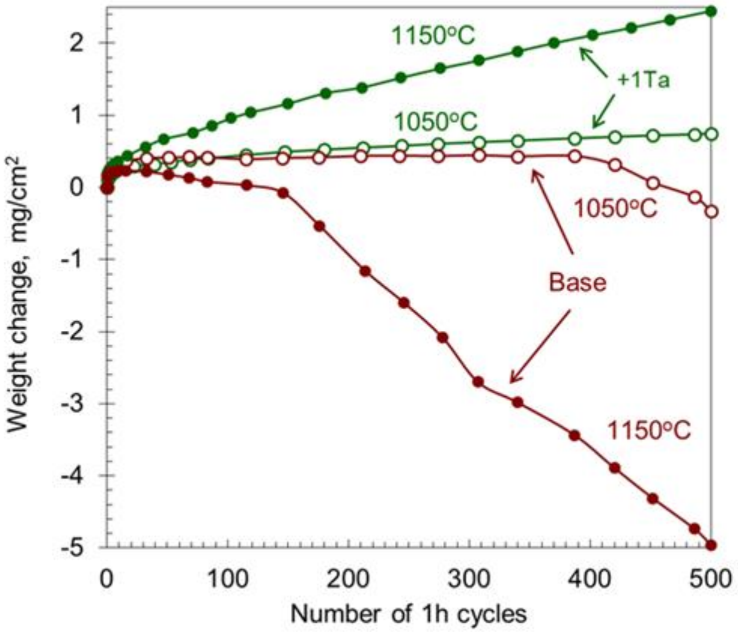
- Type II Hot corrosion at 700°C
  - Pre-oxidation at 800°C@100hrs in air prior to hot corrosion
  - 1-2 mg/cm_2 Na_2SO_4 was deposited initially and re-deposited between every cycle

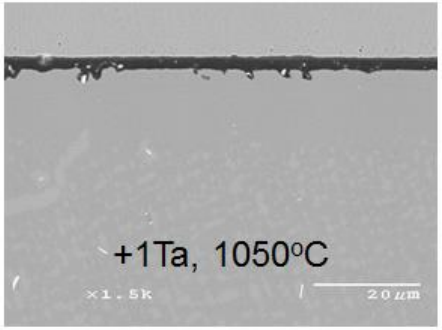
Collaboration: Brian Gleeson, U. Pitt.

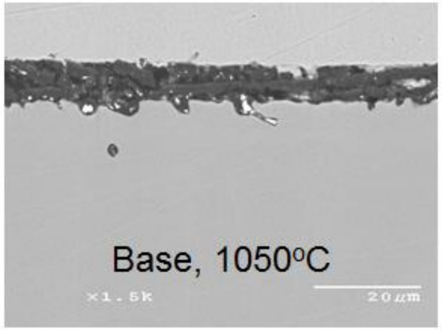
Ta Modified γ/γ' Bond Coats

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.





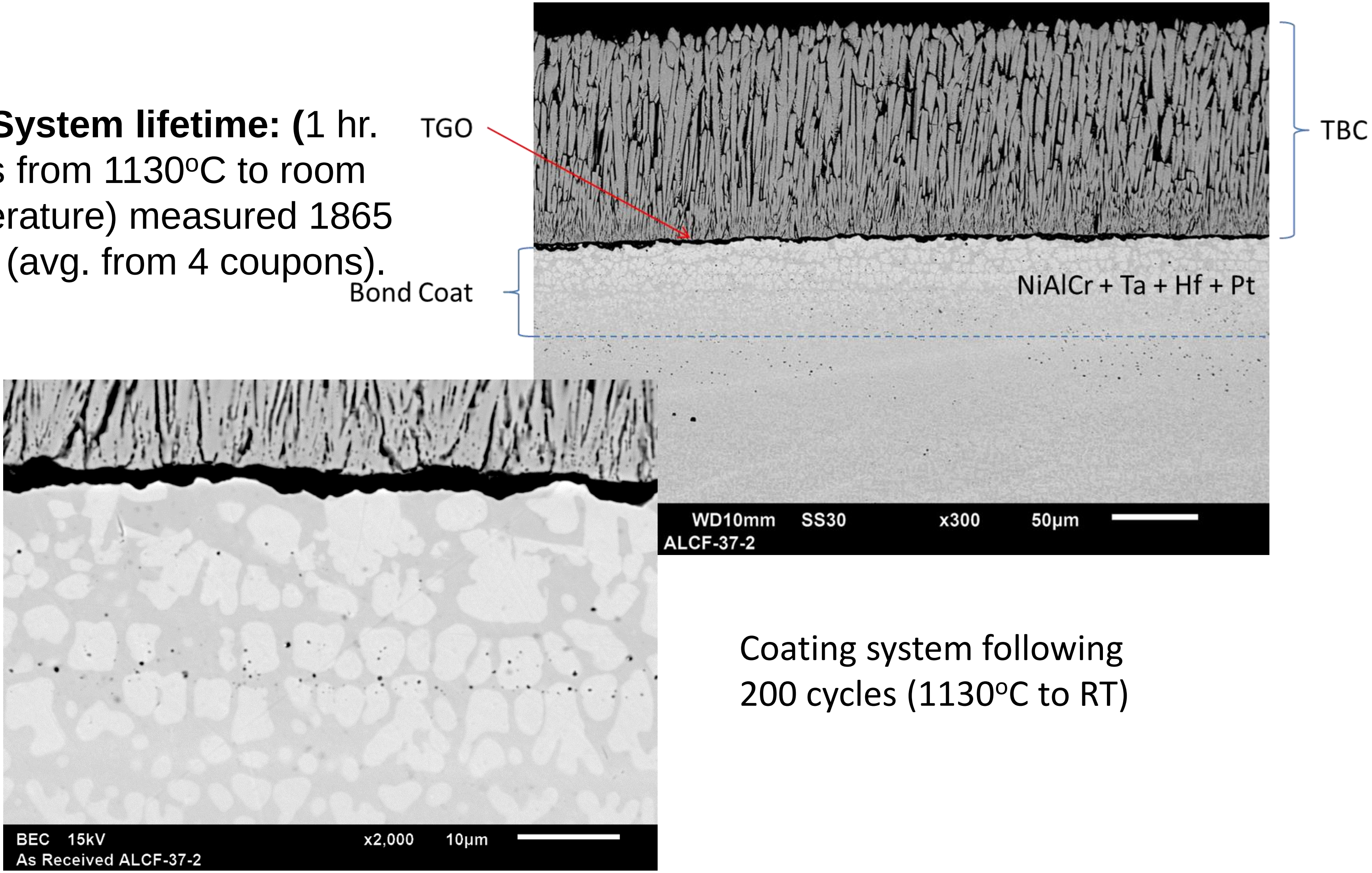


Base Composition: Ni-13Al-7.5Cr-0.1Hf-0.05Y-1Si-0.12C, at.%

- 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

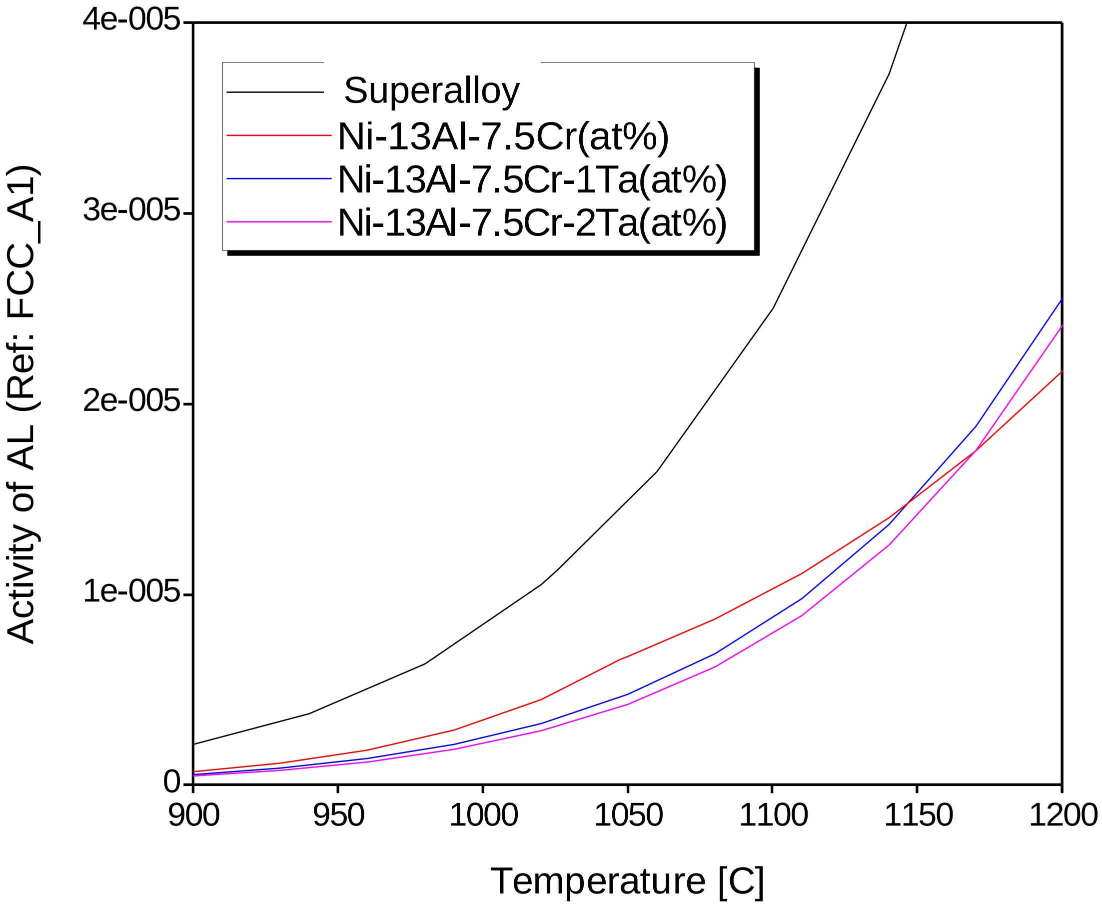
TBC System lifetime: (1 hr. cycles from 1130ºC to room temperature) measured 1865 hours (avg. from 4 coupons).



Coating system following 200 cycles (1130ºC to RT)

Funded by USAF, Ruth Sikorski

Chemical Activity Matching



Very low Al activity coatings

CompuTherm FOR MATERIALS DESIGN

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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 (with 22at.% Al – 5at.% Cr)

- 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

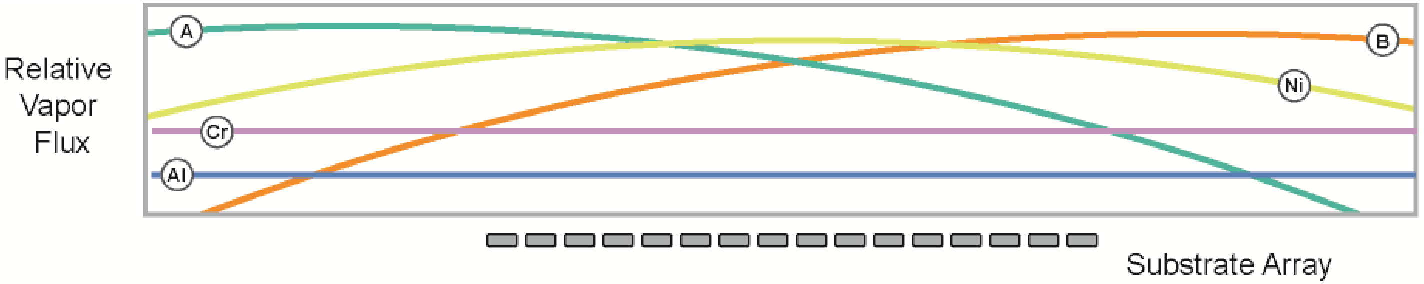
	Co	**Fe**	**Cu**	**Mn**
Co	~~Co-Co~~	~~Co-Fe~~	~~Co-Cu~~	~~Co-Mn~~
Fe	Fe-Co	~~Fe-Fe~~	~~Fe-Cu~~	~~Fe-Mn~~
Cu	Cu-Co	Cu-Fe	~~Cu-Cu~~	~~Cu-Mn~~
Mn	Mn-Co	Mn-Fe	Mn-Cu	~~Mn-Mn~~

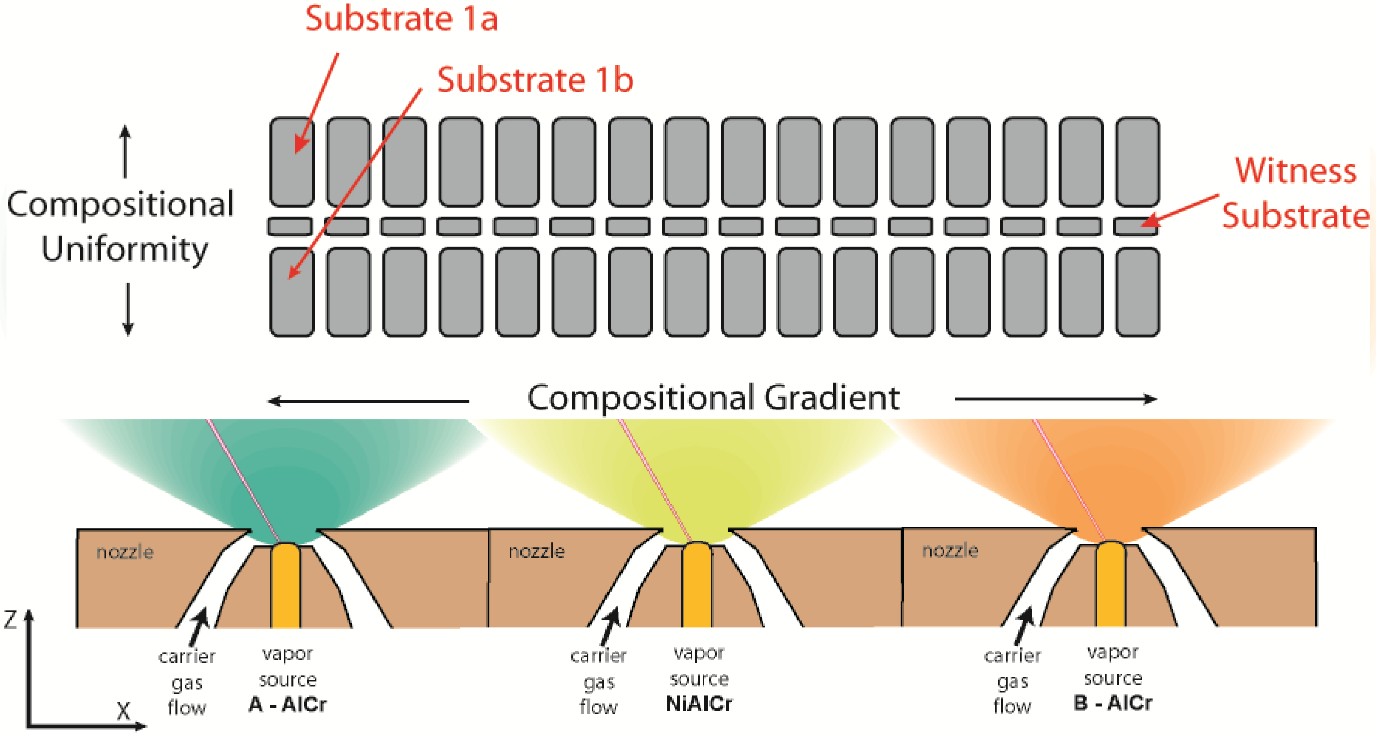
Phase II: Use both experimental and computational techniques to optimize HEA compositions of interest

Experimental: Quasi-combinatorial assessment and full bond coat application

Computational: HEA system prediction, melting point and chemical activity matching

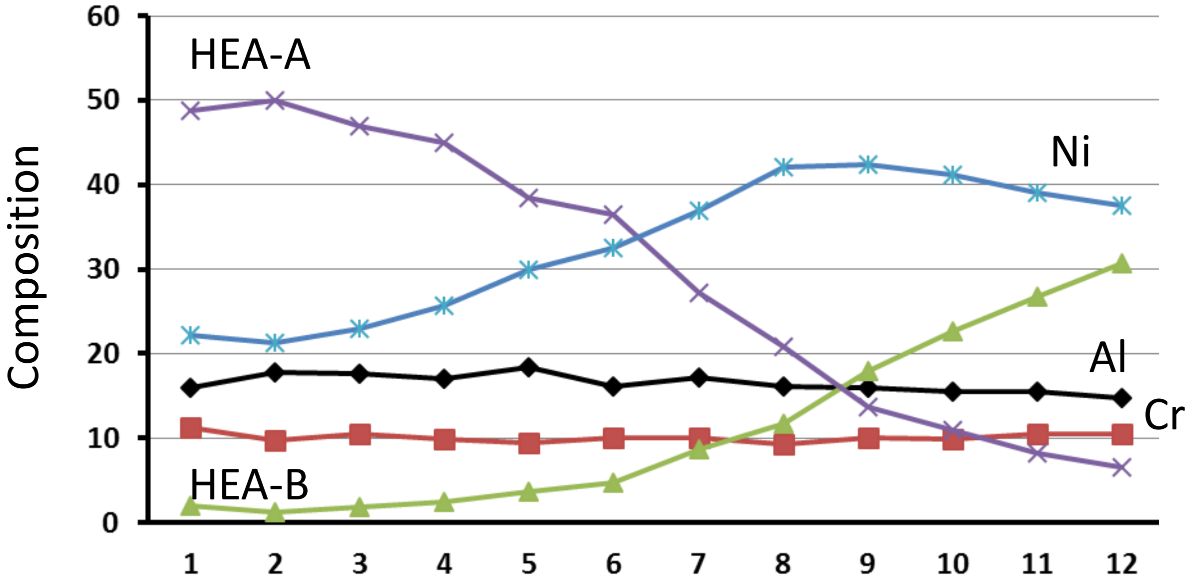
Quasi- Combinatorial Synthesis





Quasi- Combinatorial Synthesis

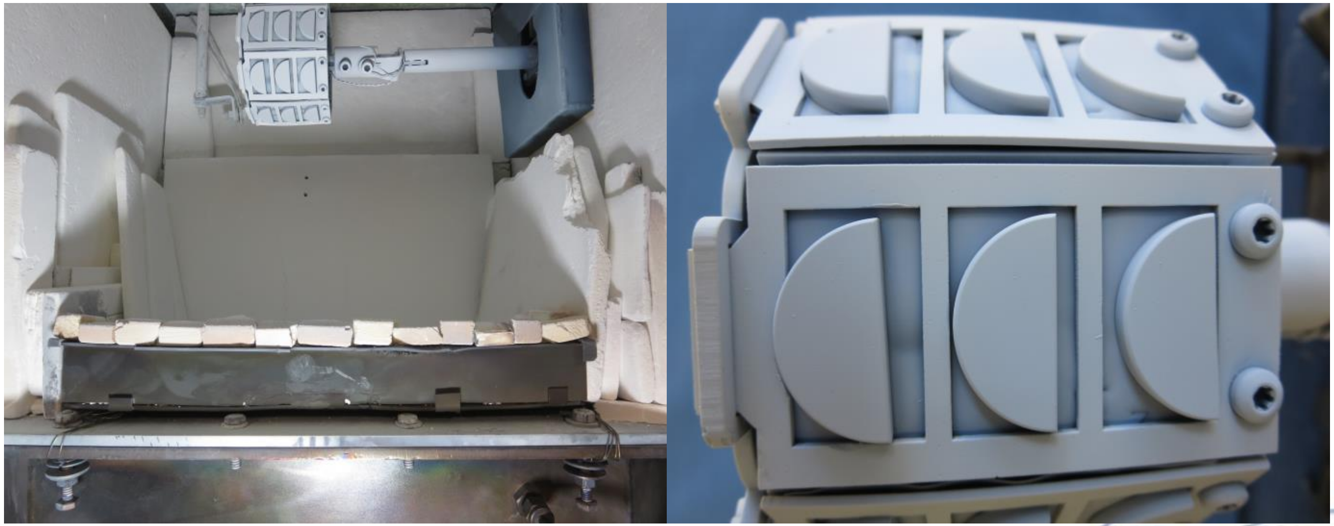
Compositional Gradient Achieved



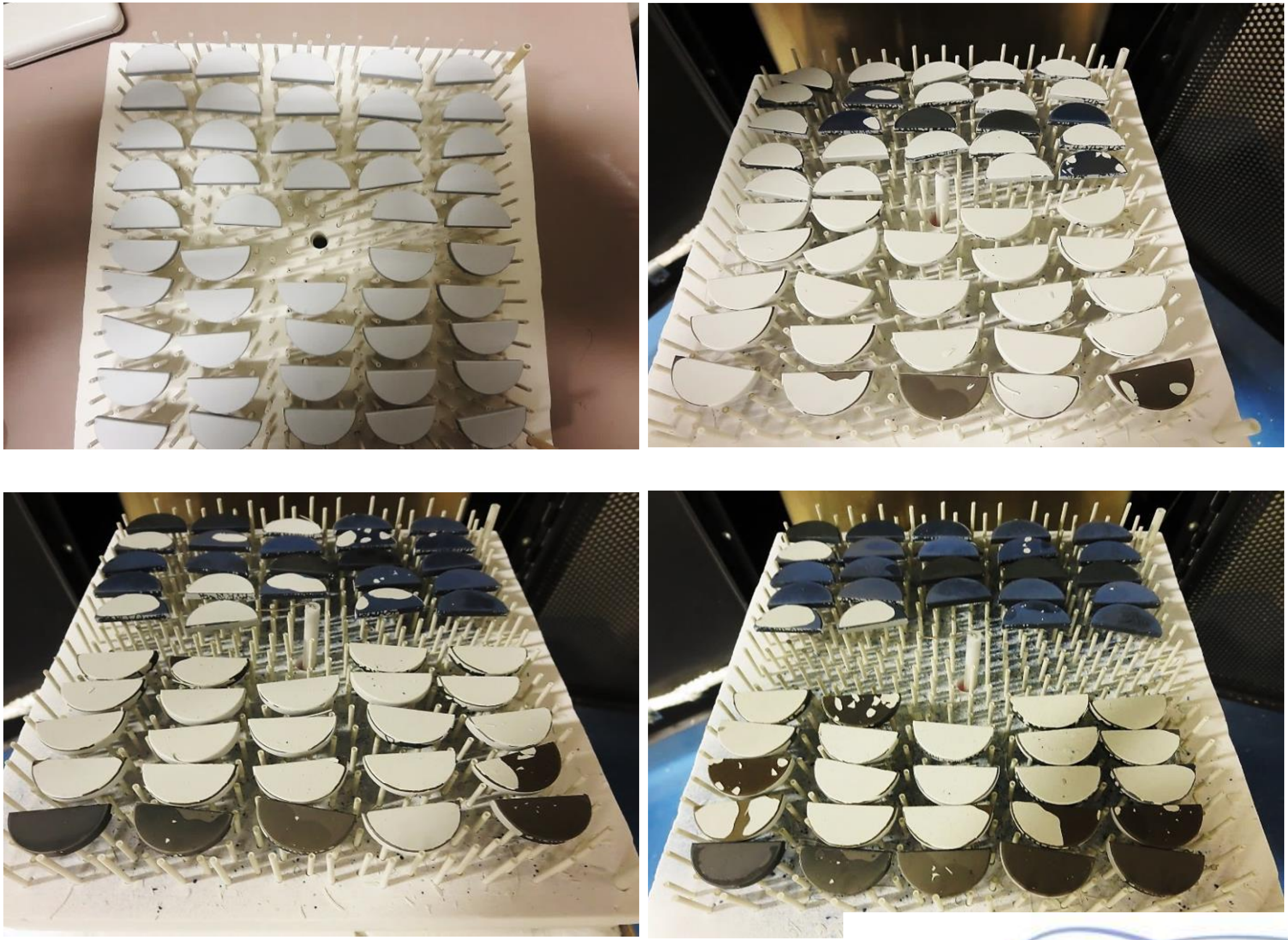
Quasi- Combinatorial Synthesis

Top Coat Application

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

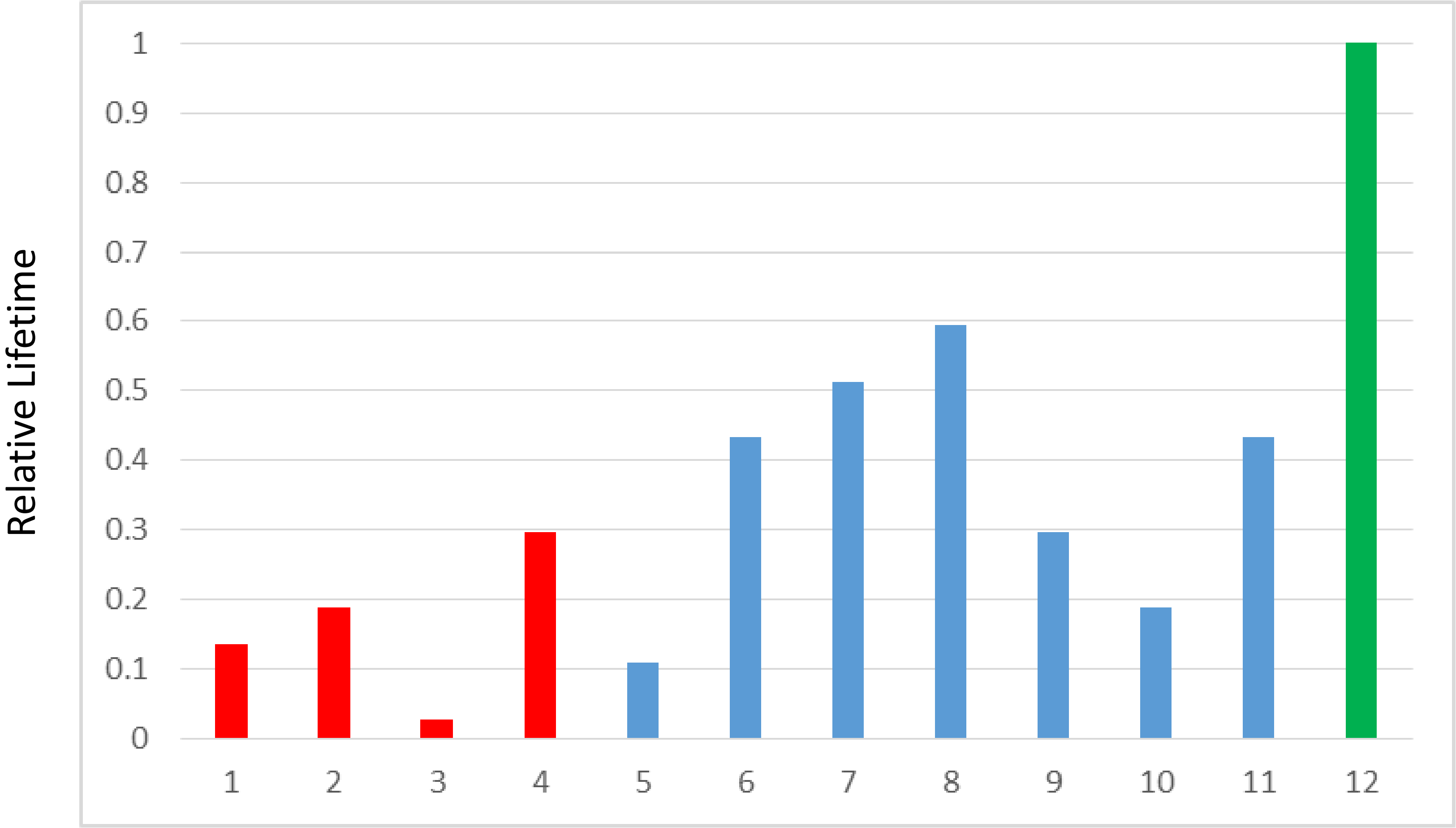


Thermal Spallation Testing



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.

Maximum life = 296 hours

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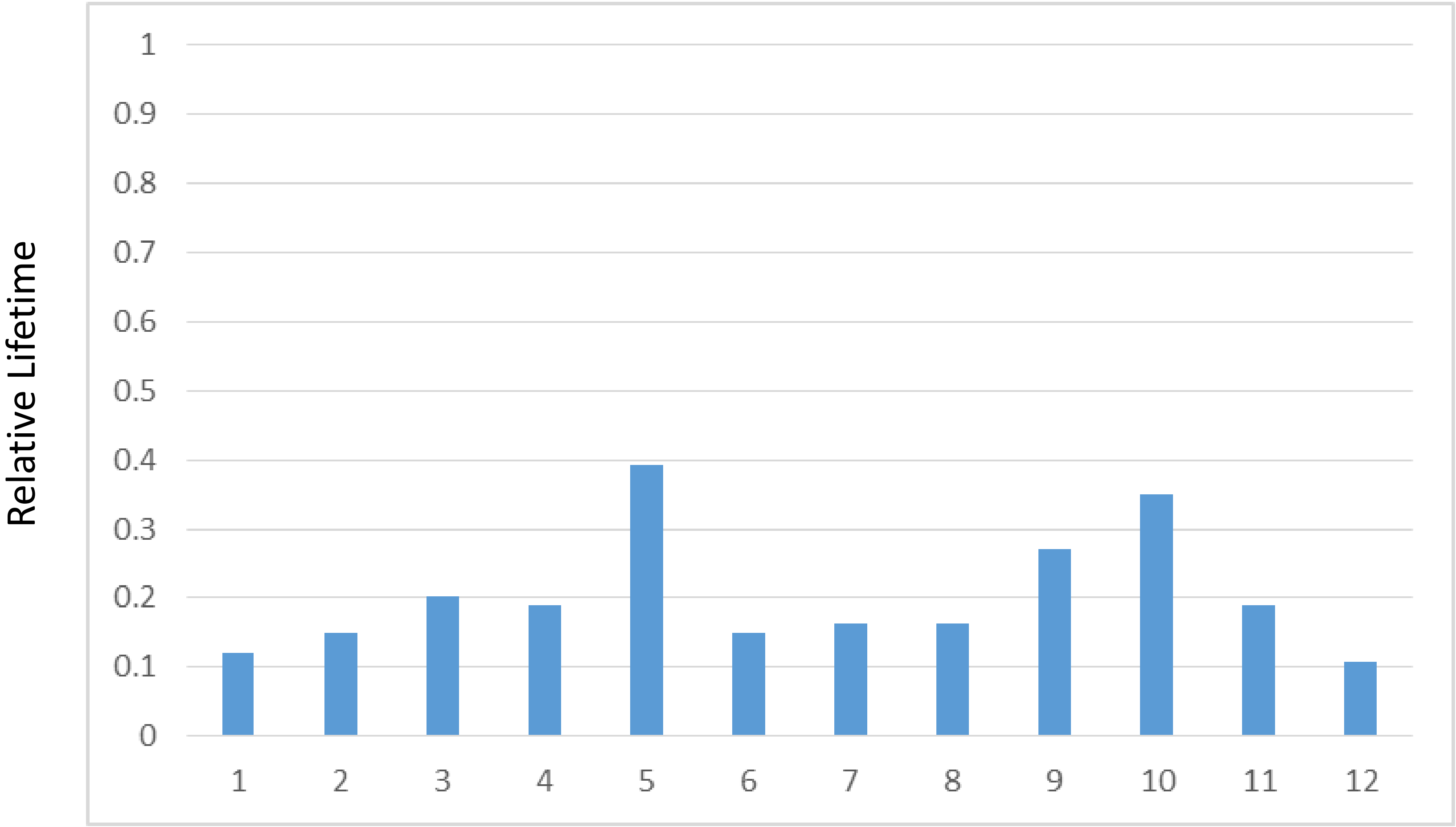
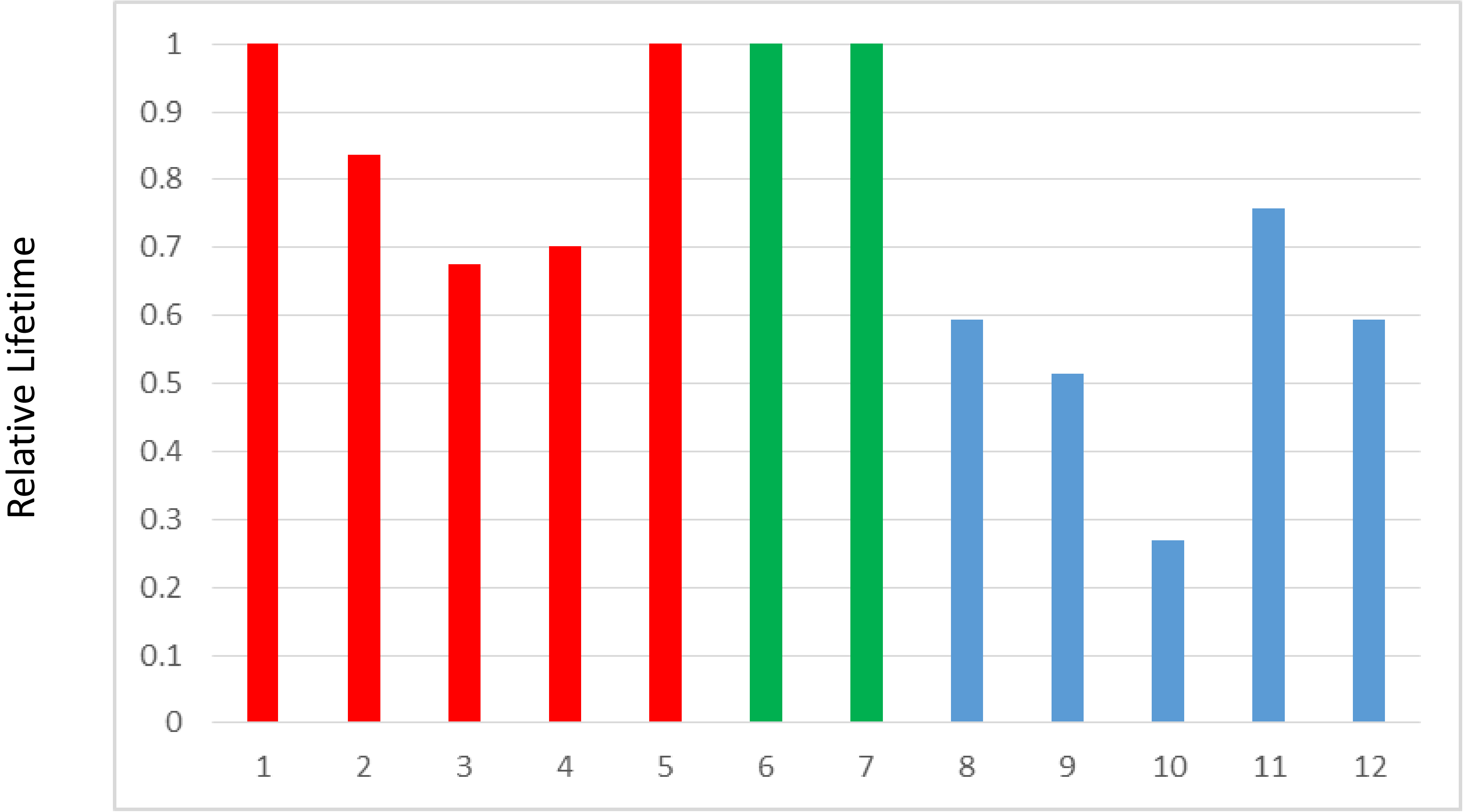
Thermal Spallation Testing

NiCuCoAlCr



Thermal Spallation Testing

NiCoFeAlCr



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.

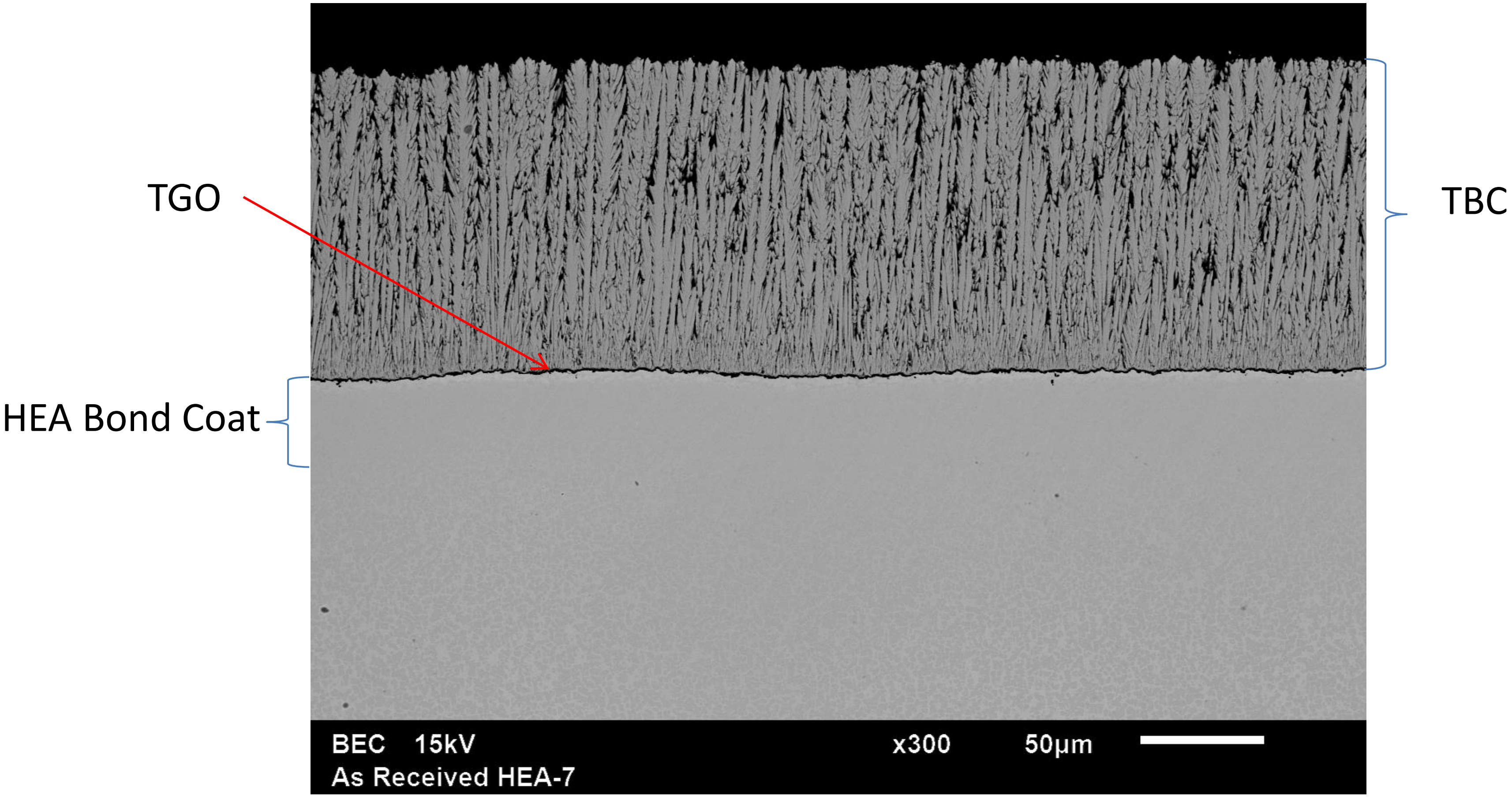
Two bond coat compositions were identified during the Phase I effort that showed promising performance in thermal spallation and oxidation testing

System A: NiCuFe-20Al-5Cr.

System B: NiCoFe-17Al-10Cr

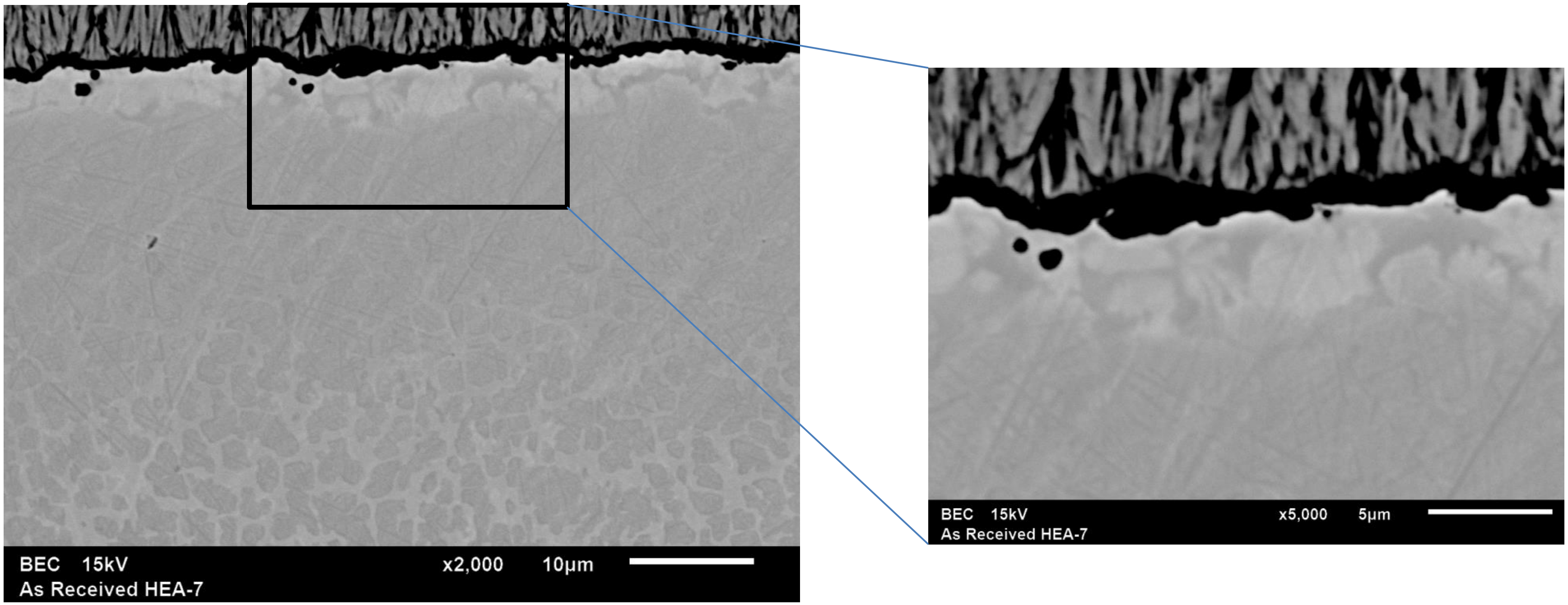
TBC Systems with HEA Bond Coats

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



TBC Systems with HEA Bond Coats

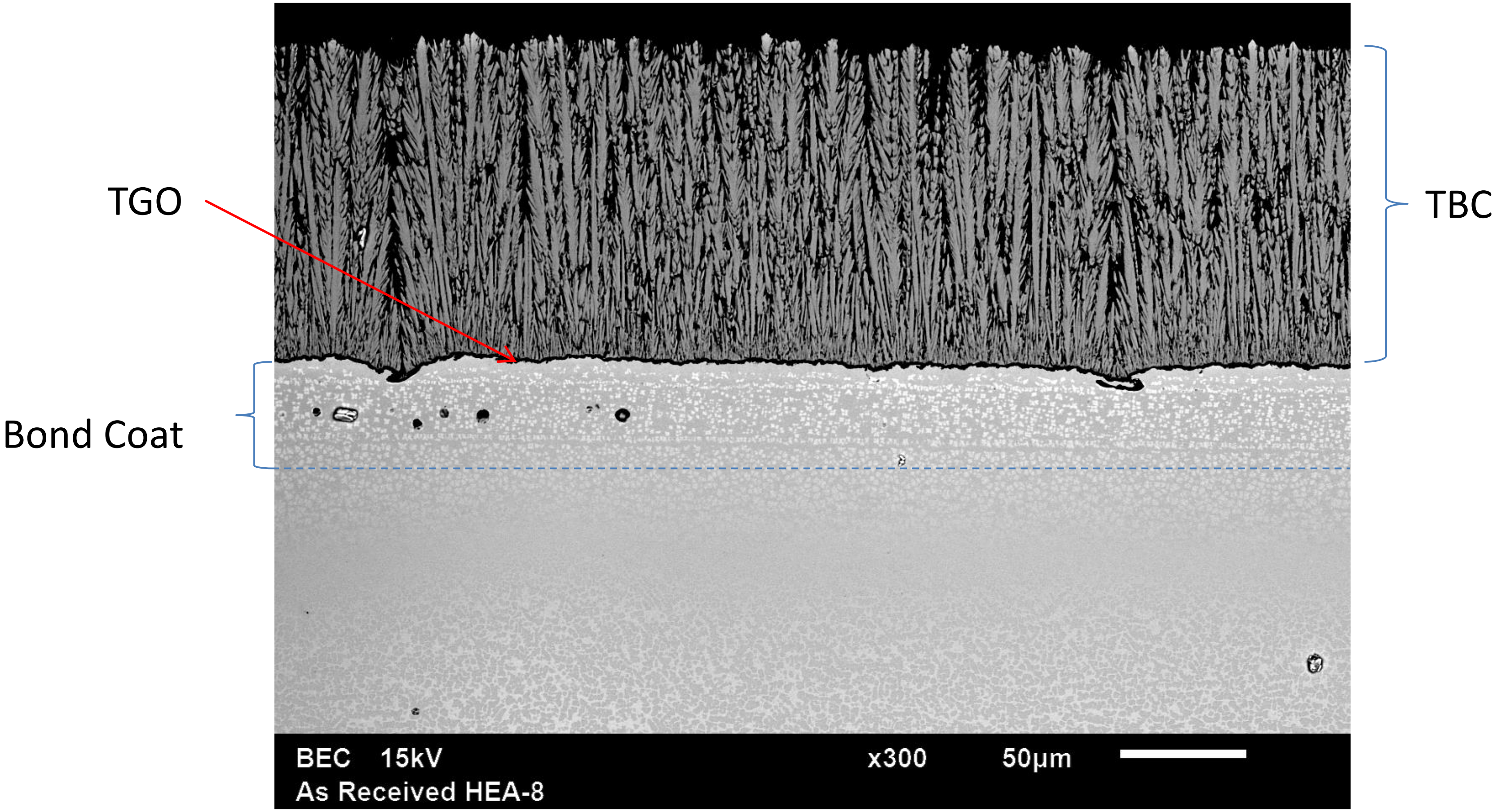
System A: NiCuFe-20Al-5Cr + Hf + Pt



XRD indicates crystalline bond coat with multiple phases present.

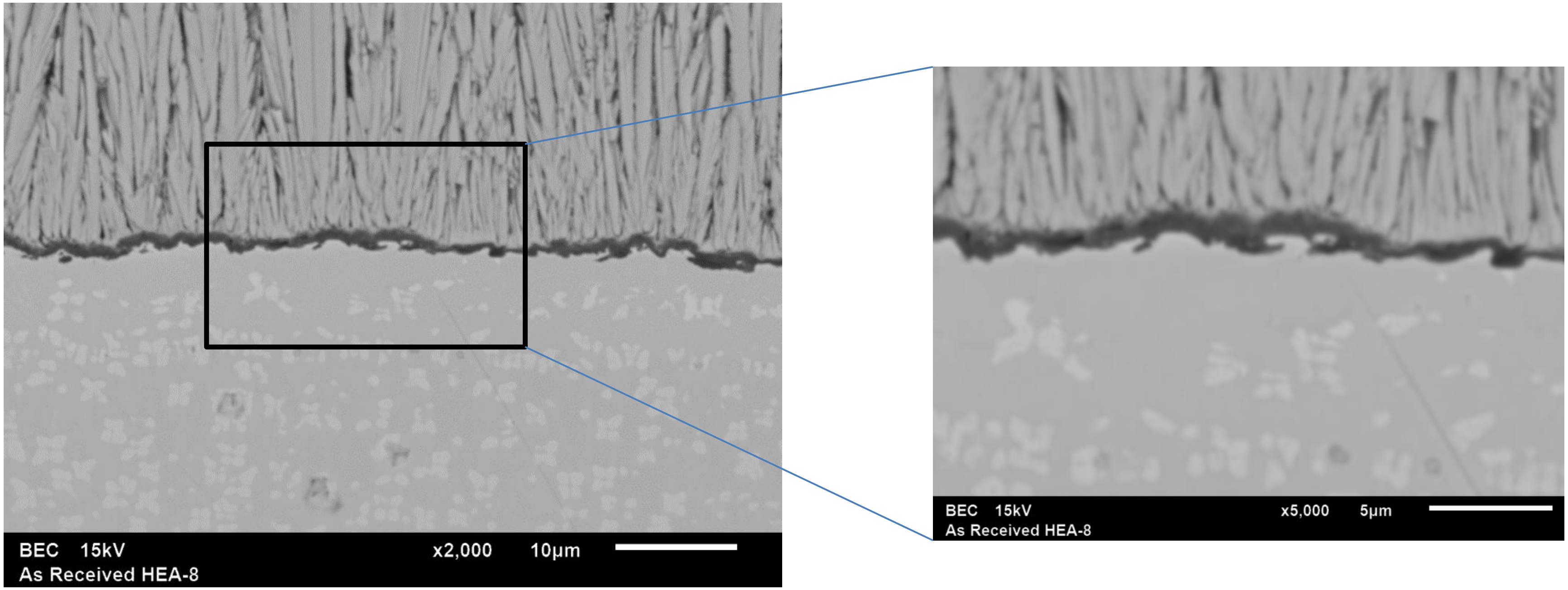
TBC Systems with HEA Bond Coats

System B: NiCoFe-17Al-10Cr



TBC Systems with HEA Bond Coats

System B: NiCoFe-17Al-10Cr



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	1512	Yes
HEA System B	1440	Yes
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

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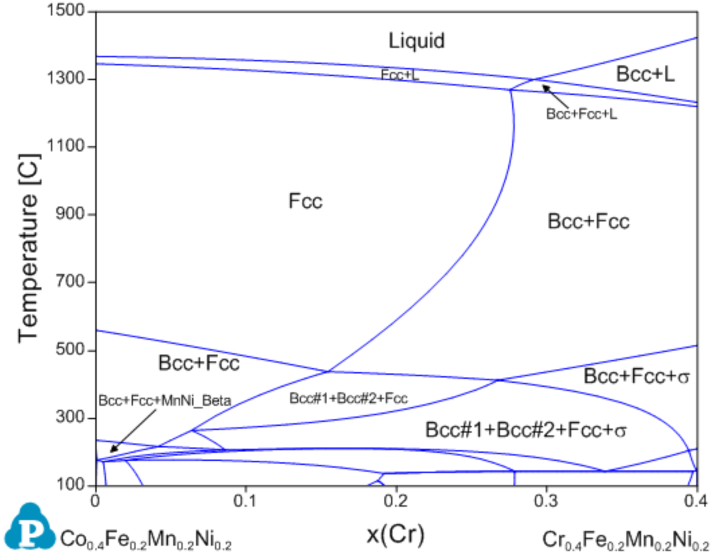
SOFTWARE

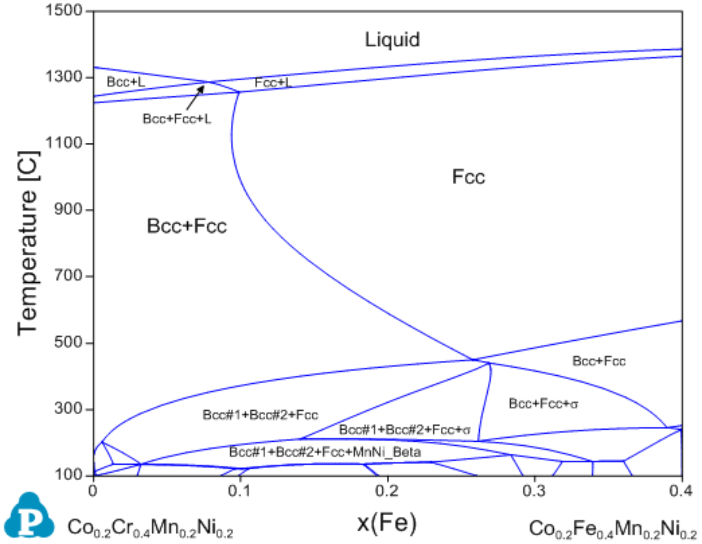
CompuTherm, LLC

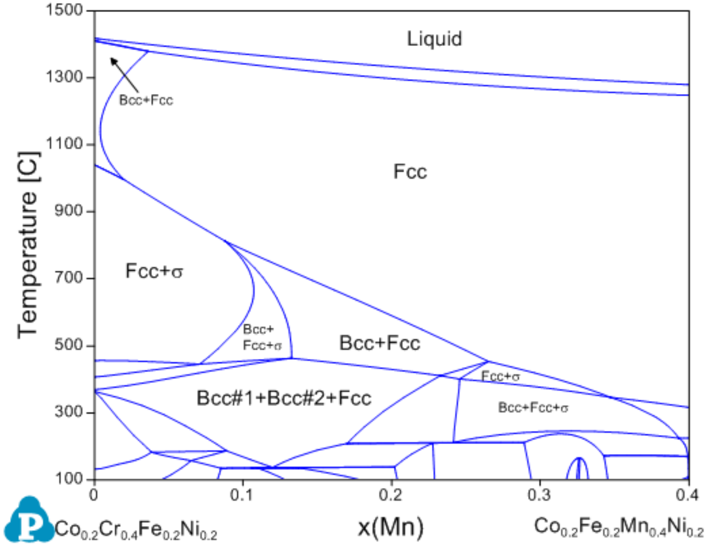
437 S. Yellowstone Drive, Madison, WI, USA

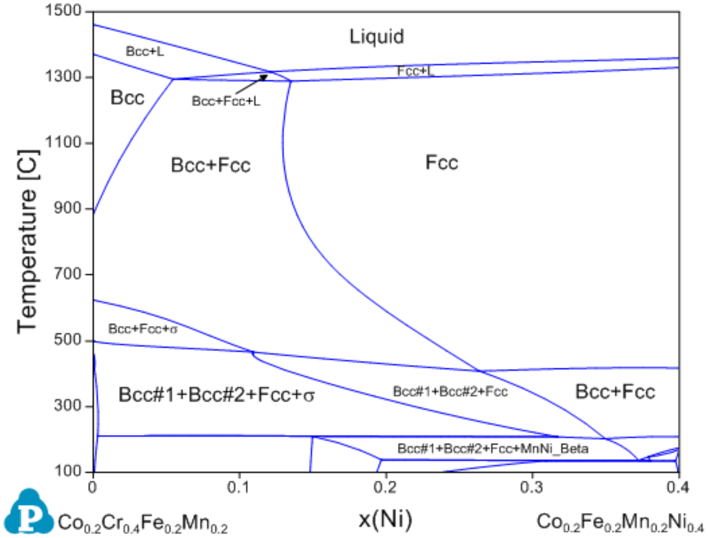
http://www.computherm.com

Cr-Mn-Co-Fe-Ni Isopleth Sections



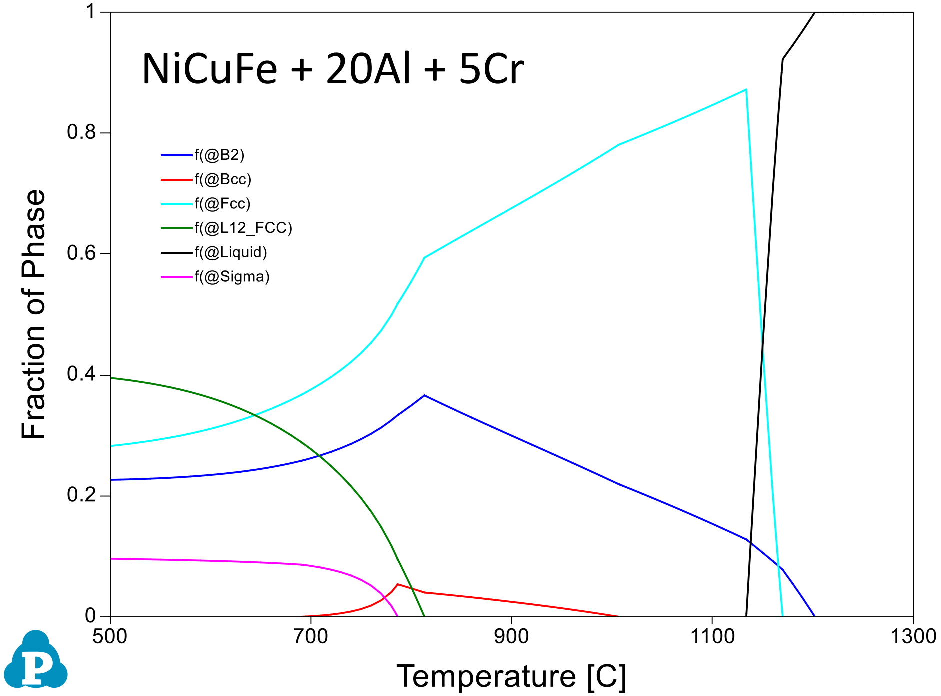


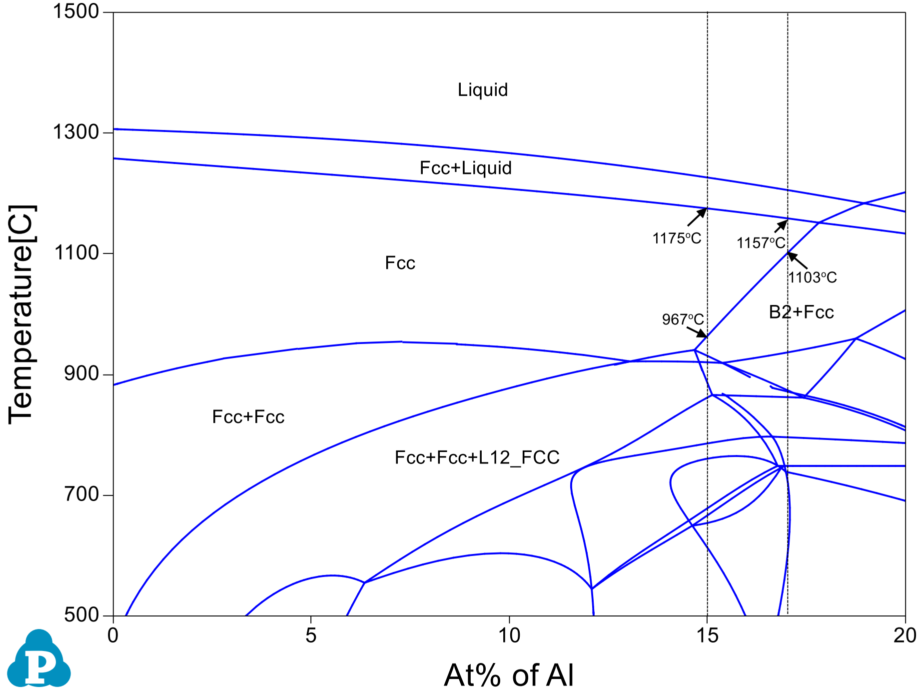




Isopleths calculated for the Cr-Mn-Co-Fe-Ni system. It is seen, FCC is stable in wide composition and temperature. This is why single fcc HEAs were developed in this 5-component system

HEA Bond Coats - CalPHAD



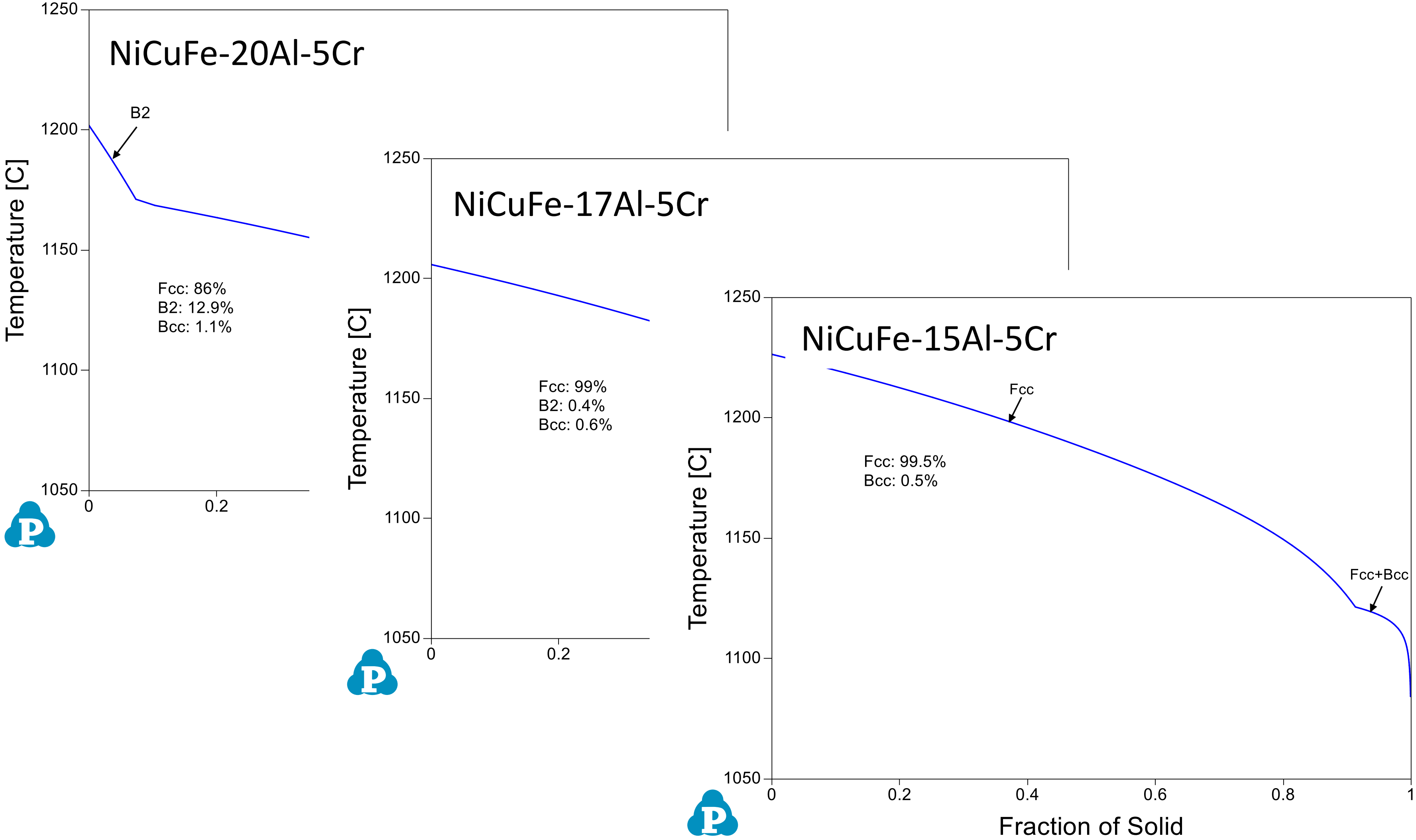


A line calculation was performed for System A NiCuFe + 20Al + 5Cr (at%) alloy at varying temperature from 500°C to 1300°C.

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.

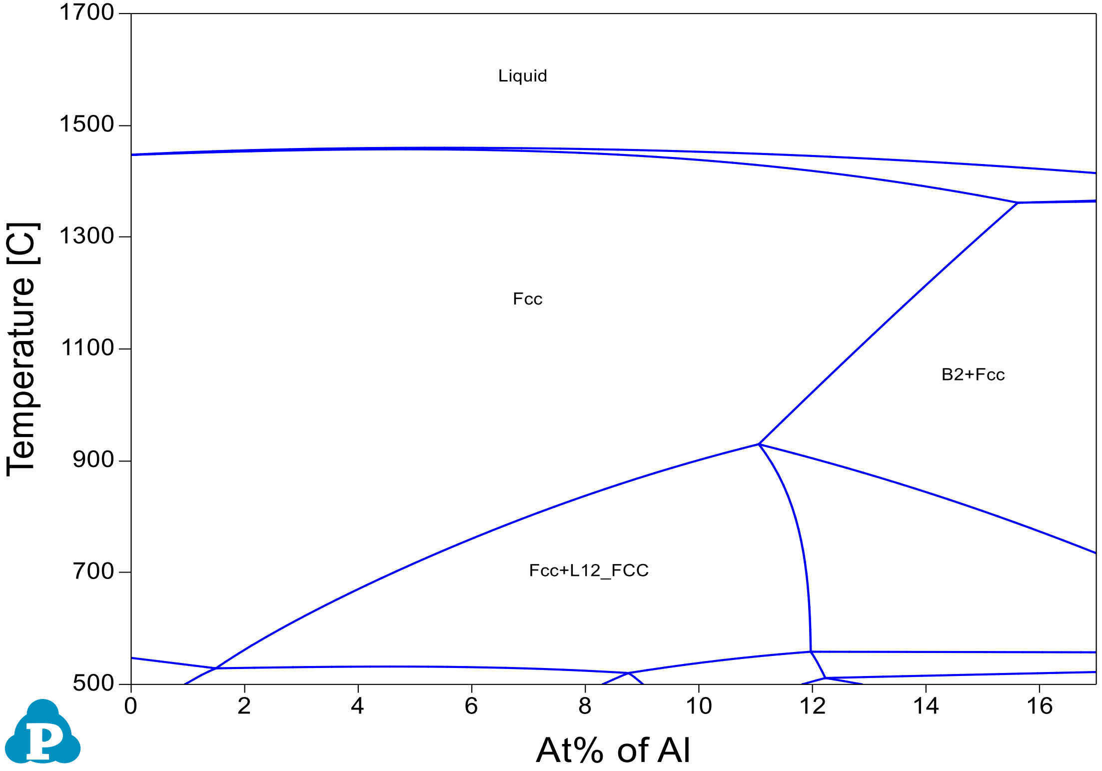
HEA Bond Coats



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

HEA Bond Coats

System 2: NiCoFe-xAl-10Cr



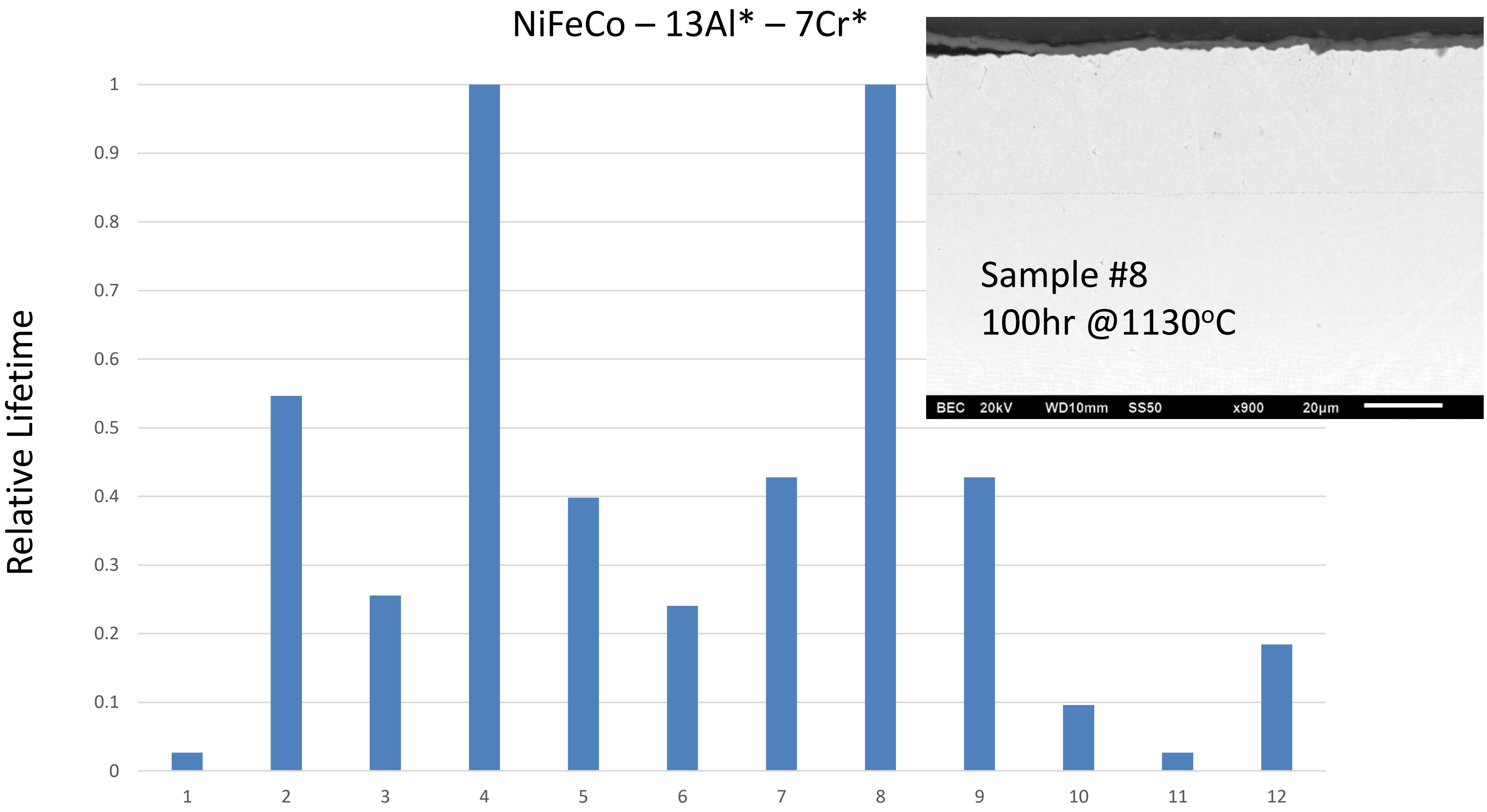
FCC is stable in wide composition and temperature range. Good potential for HEA formation if Al content reduced.

HEA Bond Coats

- Additional combinatorial libraries were manufactured having lower Al contents (13Al- 7.5Cr vs. 22Al – 5 Cr at%)

- Mn additions were enabled

HEA Bond Coats



NiFeCo – 13Al* – 7Cr*

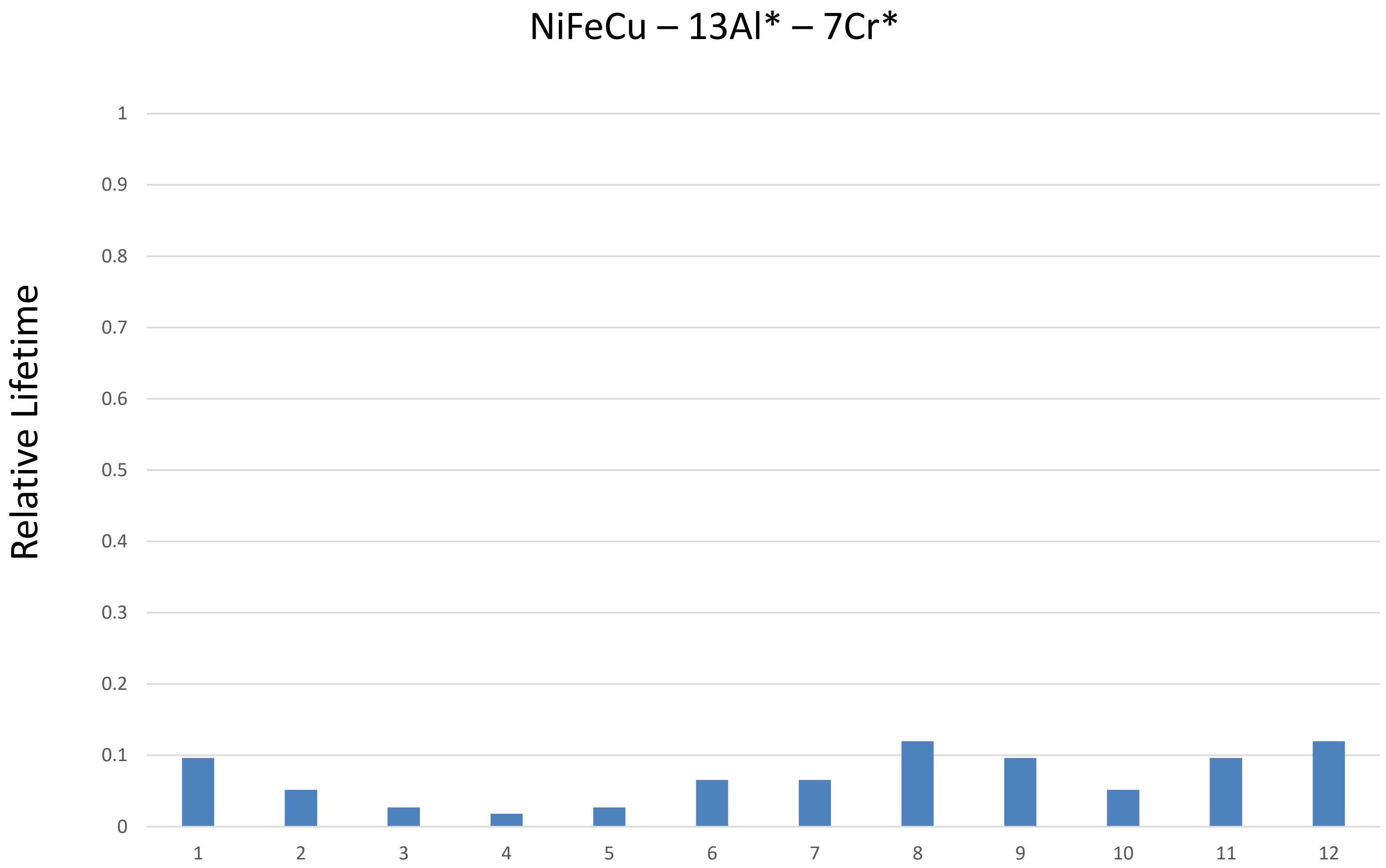
Sample #8
100hr @1130^{o}C

Maximum life = 1010 hours (without failure)

Sample 4, 8 = Completed 2500 cycles without failure

* Values in the source rods

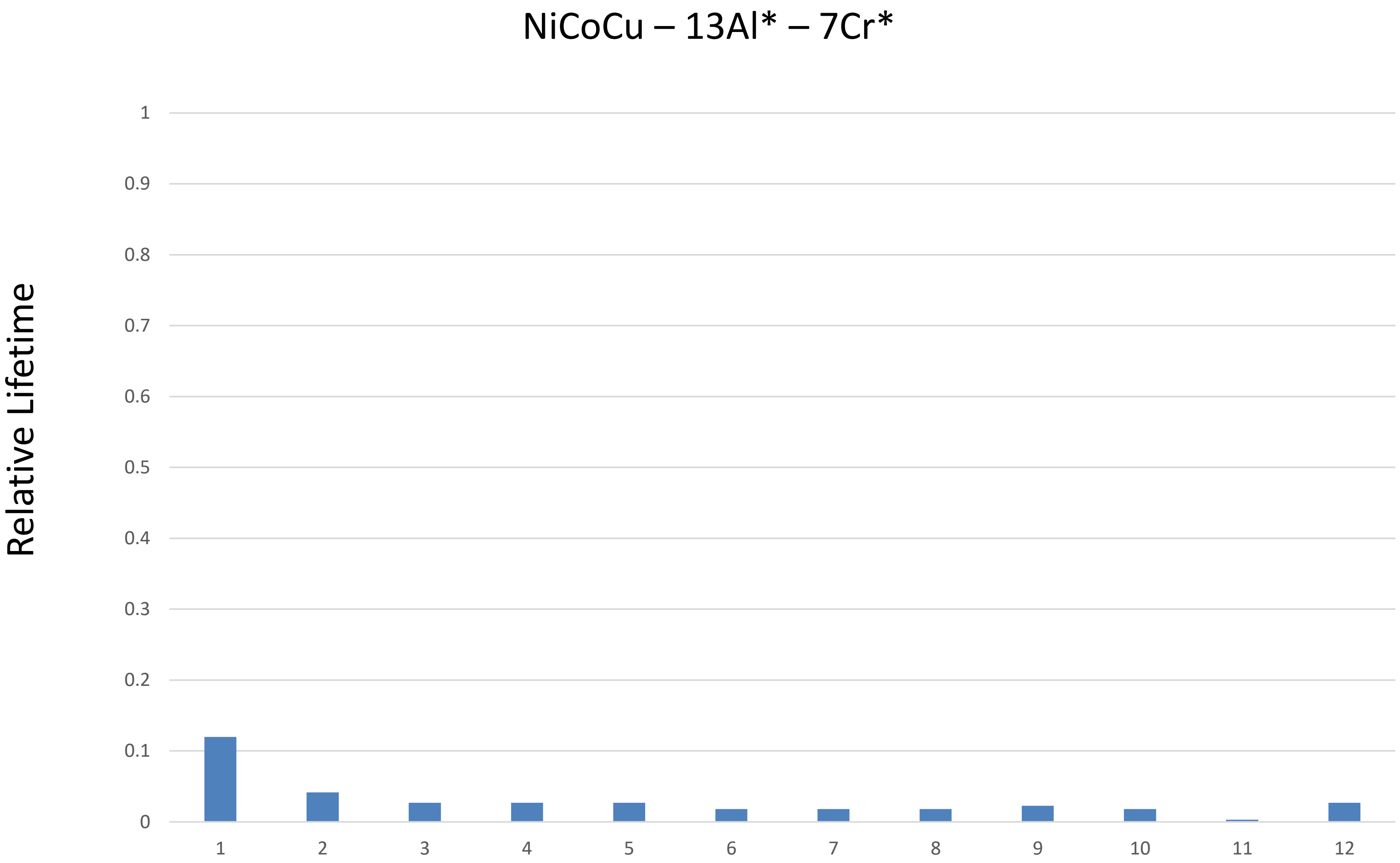
HEA Bond Coats



Maximum life = 1010 hours (without failure)

* Values in the source rods

HEA Bond Coats



Maximum life = 1010 hours (without failure)

* Values in the source rods

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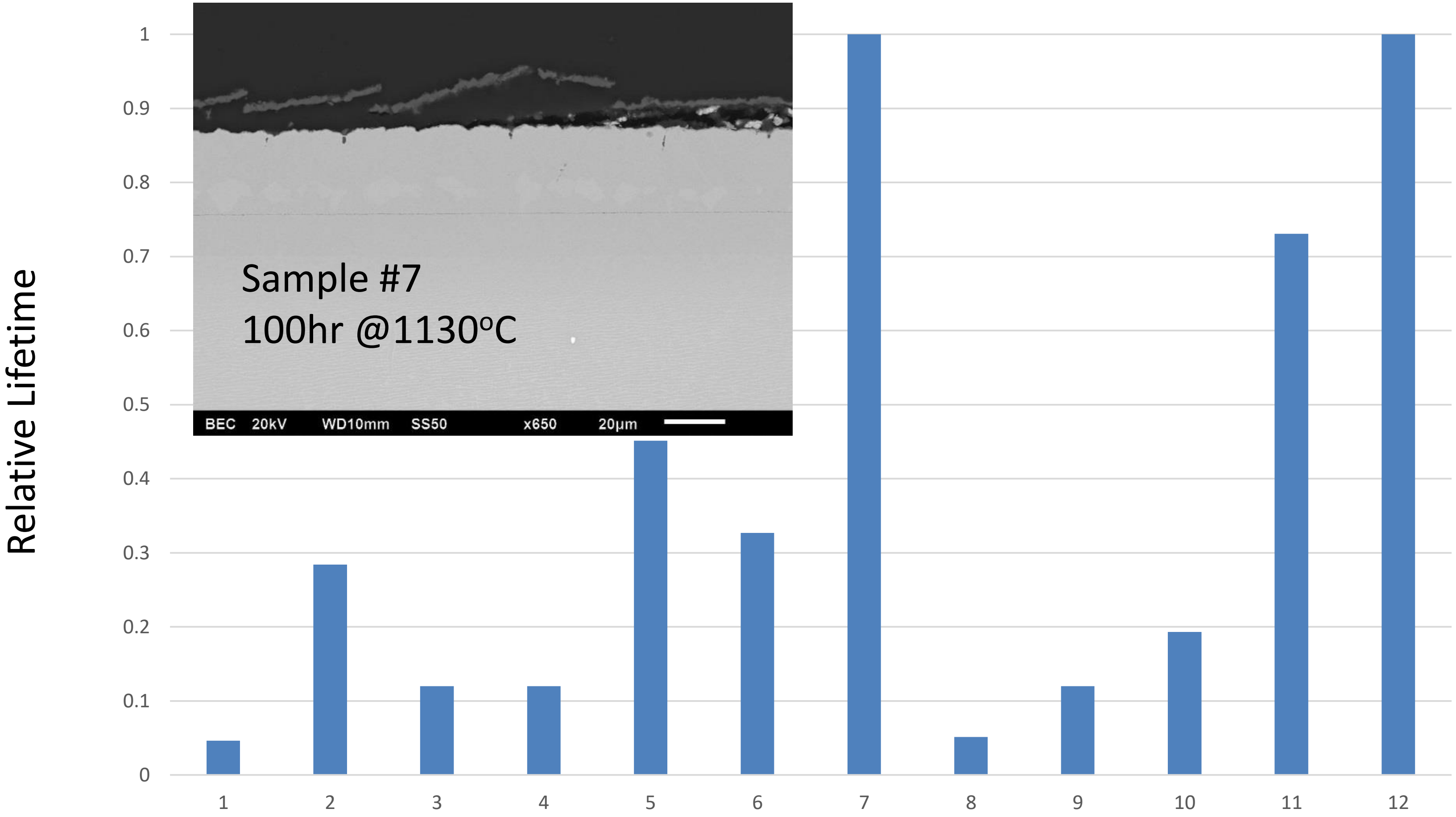
HEA Bond Coats



NiCoMn – Al* – Cr

Sample #7
100hr @1130°C

Maximum life = 1010 hours (without failure)

Sample 7, 12 = Failed after 1698 cycles

* Higher Al content due to use of original MnAlCr source

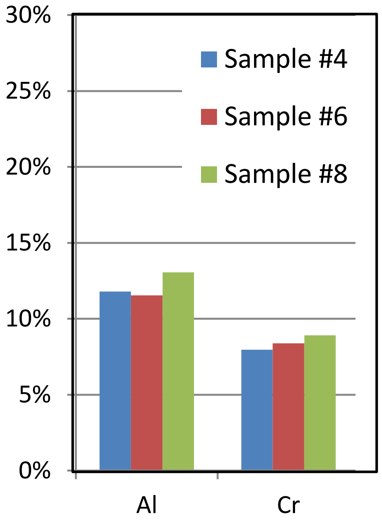
- System likely two phase due to higher Al content

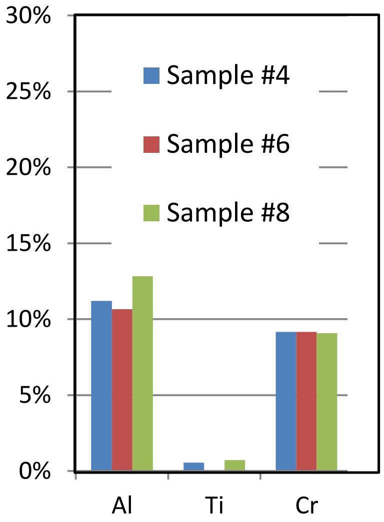
HEA Bond Coats

As Deposited

100hr @1130°C

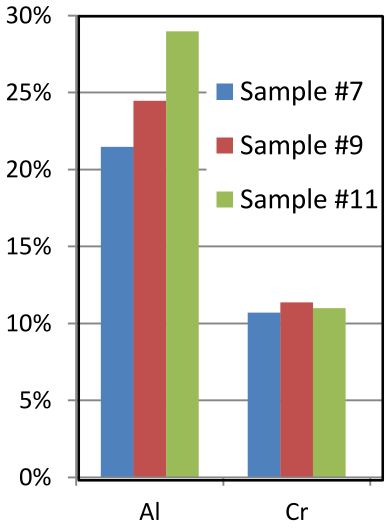
NiFeCoAlCr

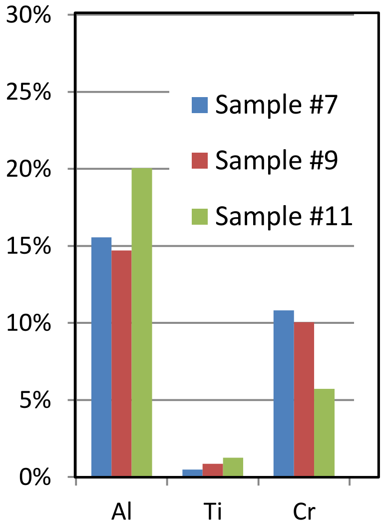




- Very low Al, Cr interdiffusion
- Ni,Fe,Co will interdiffuse with substrate

NiCoMnAlCr

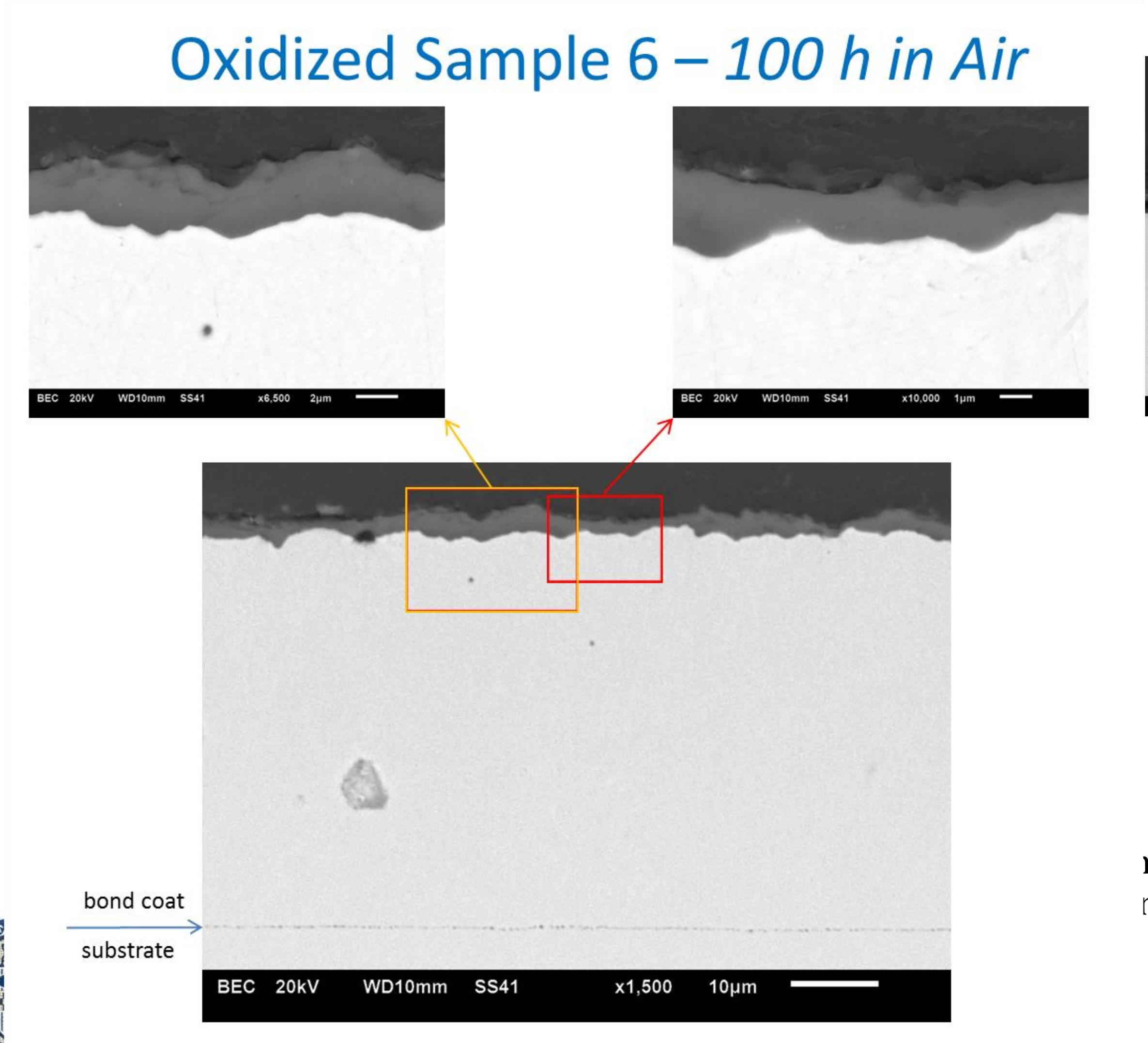




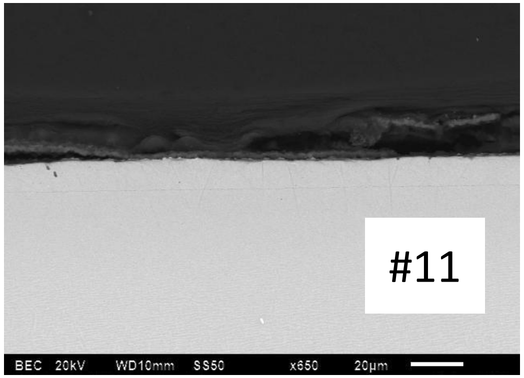
- Higher Al, Cr levels with substrate interdiffusion
- Ni,Fe,Co will interdiffuse with substrate

HEA Bond Coats

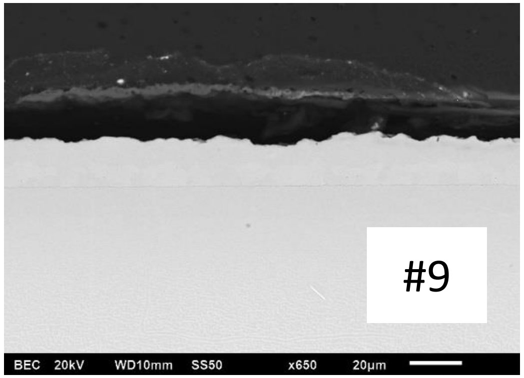
Alumina Scale Adherence after Testing for 100 h@1130 °C



Oxidized Sample 6 – *100 h in Air*



#11



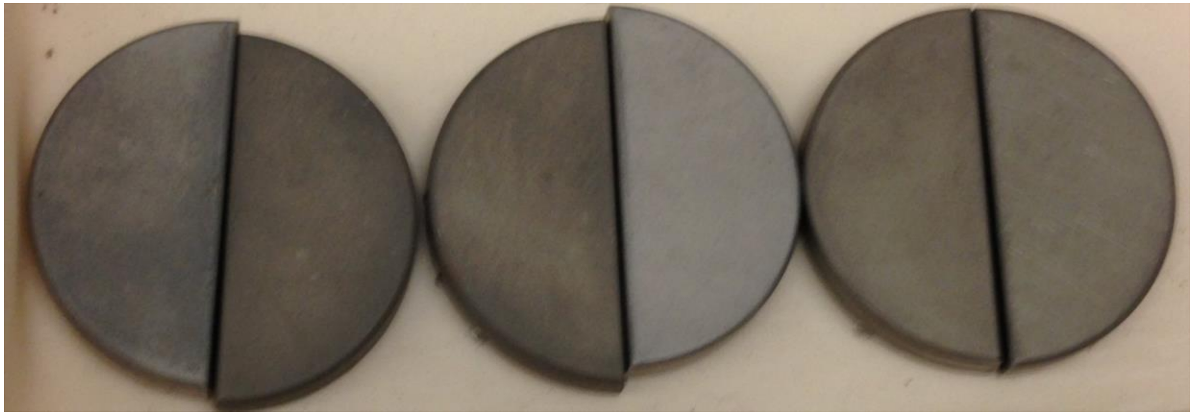
#9

ples #8, #11, #4, #7 and #9. Even
ng surface. Typical alumina scale
limited locations in Sample #9.

HEA Bond Coats

Ni**Fe**CoAlCr: Samples #4, #6, #8

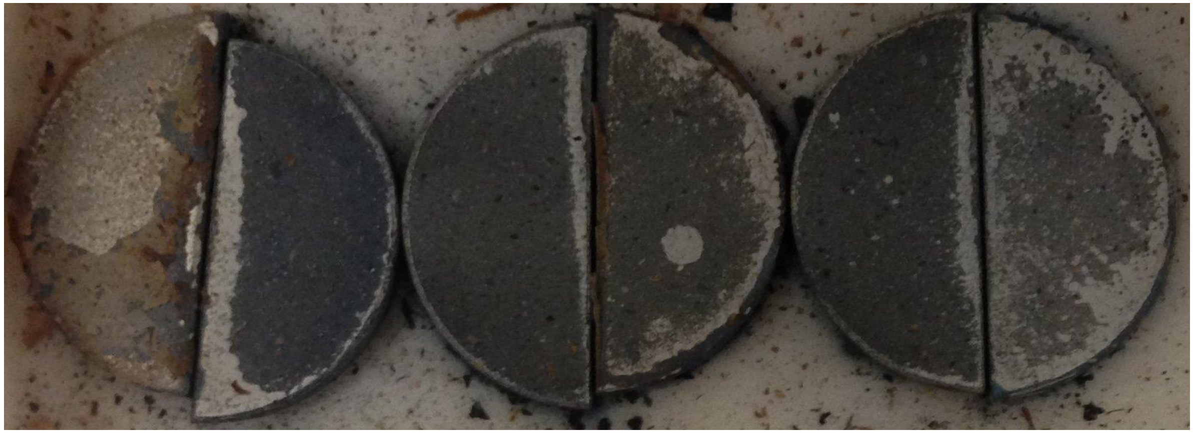
NiCo**Mn**AlCr: Samples #7, #9, #11



Before Test:

Non-uniform surface appearance on some samples.

#9 #4 #6 #11 #8 #7

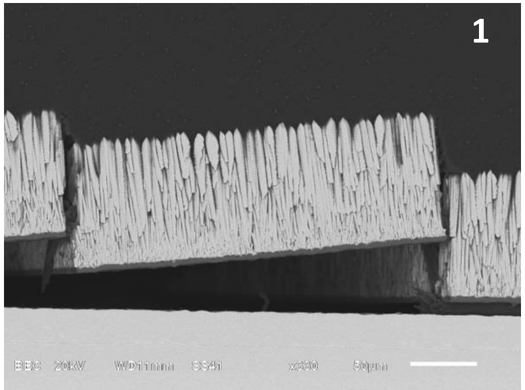


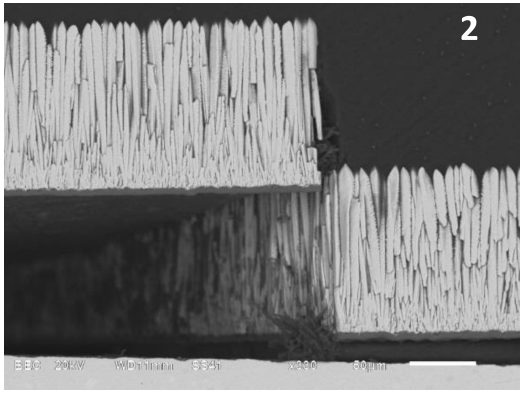
After Test
100 h@1130 ^{o}C:

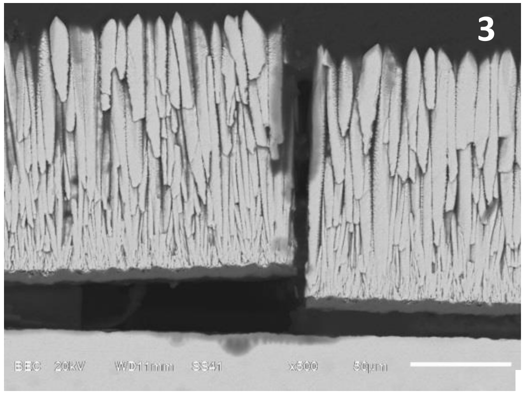
SEM images reveal a large amount of alumina-scale spallation from Samples #9 and #7.

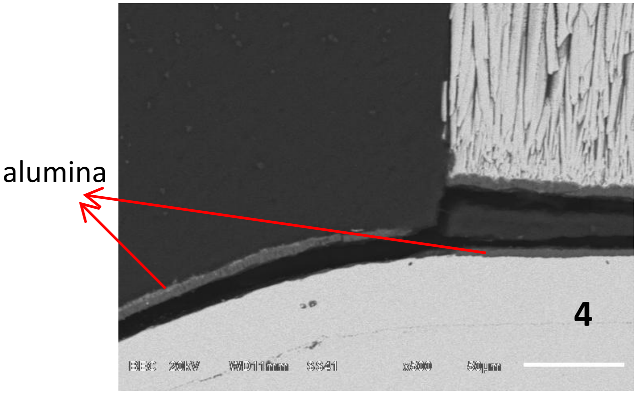
HEA Bond Coats

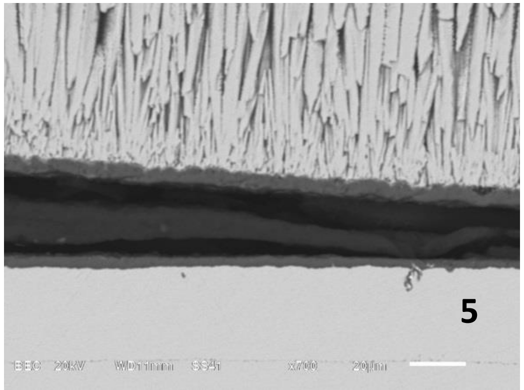
TBC spallation of an NiFeCoCrAl sample after cyclic oxidation ~2500 cycles@1130^{o}C

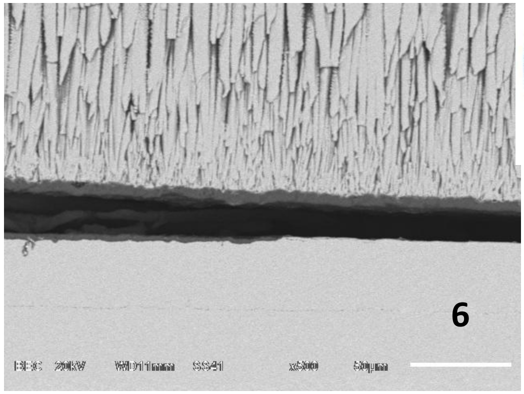








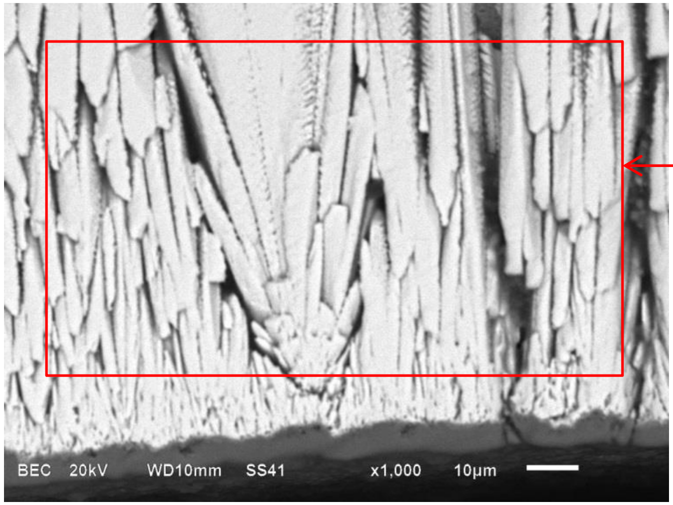




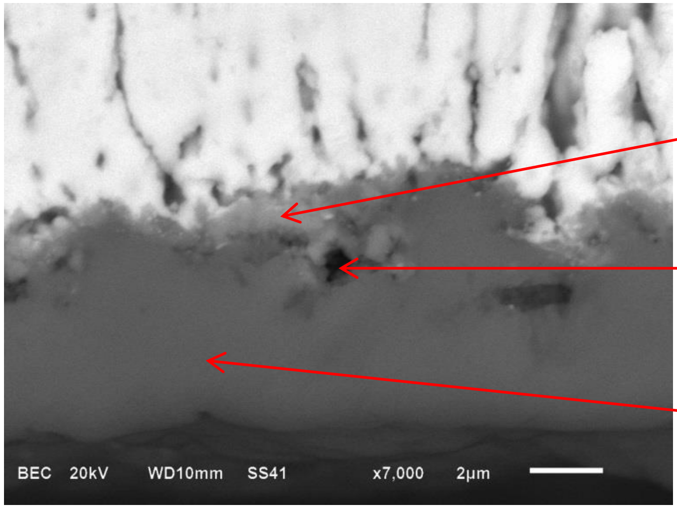
- Figures 1-2 show that the TBC spalled in sections. No oxide on the surface of the bond coat was found, indicating that the TBC spallation occurred during cooling or subsequent post-test handling.
- Figure 3 shows that in a rare case there is some oxide (NiO) on the surface of the bond coat at the split of TBC.
- Figures 4-5 shows that at a sample edge, besides the alumina scale spalled from the bond coat, a new thinner alumina scale had formed on the bond-coat surface, implying this part of the TBC spalled at temperature or during heating.
- Figure 6 is an extension of Figure 5. On the right the new alumina scale on the bond coat surface is not present.

HEA Bond Coats

TBC spallation of an NiFeCoCrAl sample after cyclic oxidation ~2500 cycles@1130^{o}C



O	65%
Zr	35%



O	60%
Al	27%
Co	2%
Ni	6%
Zr	5%

C	55%
O	28%
Al	18%

O	56%
Al	44%

- Alumina scale has good adherence to the TBC. No significant spallation between alumina and TBC is found.
- Some horizontal cracks inside alumina exist but across in the interface.
- Some vertical cracks inside alumina appears, which looks to be associated with the microstructure of TBC.

HEA Bond Coats

Can the size of the FCC field be altered by alloying?

Can the melting point be modified?

- The effect of Co, Mn, Si, and Ti on the Ni-xAl-Cu-Fe-5Cr (at%) isopleths have been explored.

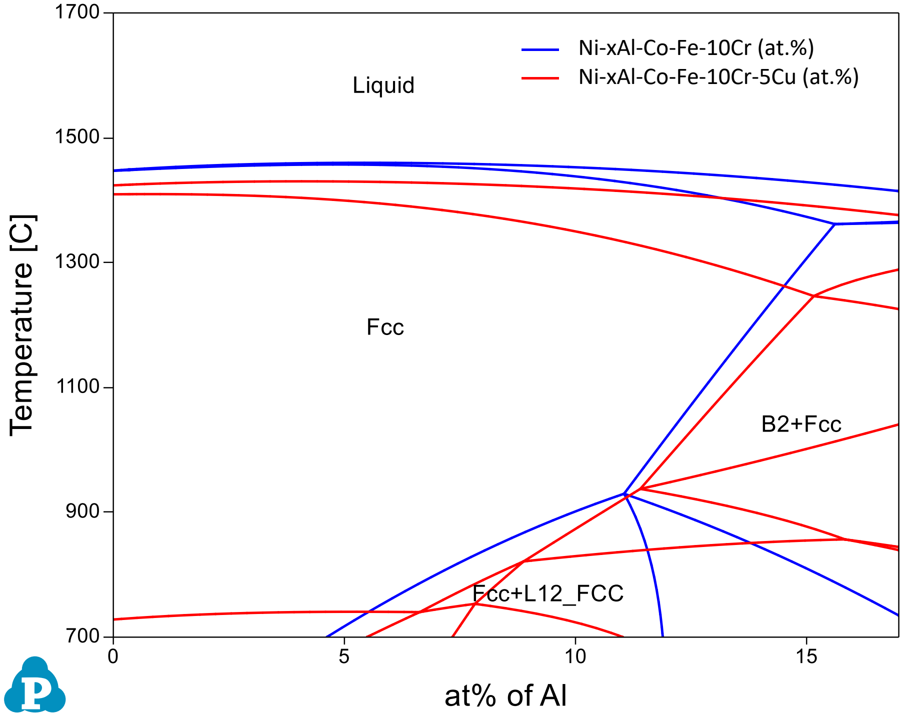
- The effect of Cu, Mn, Si, and Ti on the Ni-xAl-Co-10Cr-Fe (at%) isopleths have been explored.

- The phase boundary with 5 at% of the additional element is represented by the red color, which is superimposed to the original isopleths represented by the blue color.

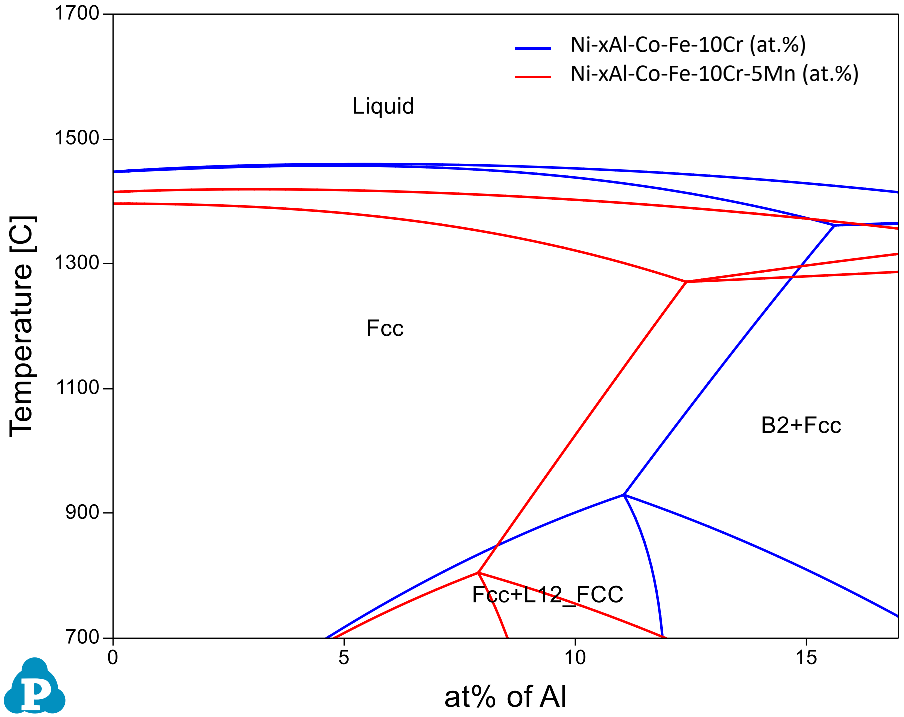
- Note that, since the purpose is to understand the effects of these elements on the liquidus, solidus, and the Fcc phase region, the diagrams are plotted in the temperature range of 900-1400^{o}C.

HEA Bond Coats

Ni-Co-Fe-xAl-10Cr-X (at%)



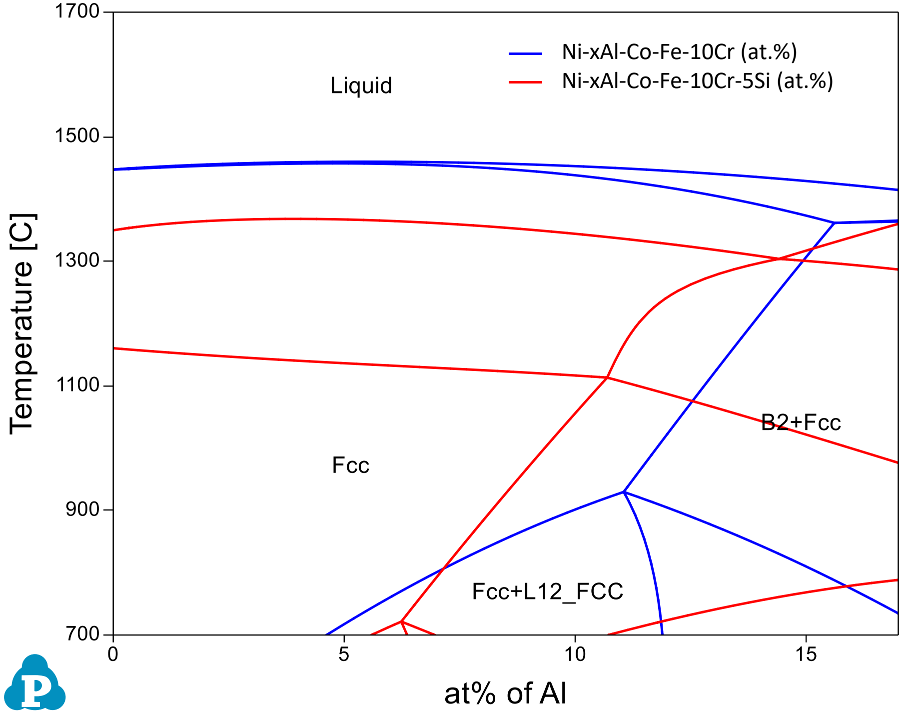
Effect of 5 at% Cu on the isoplethal section of Ni-xAl-Co-Fe-10Cr (at%)

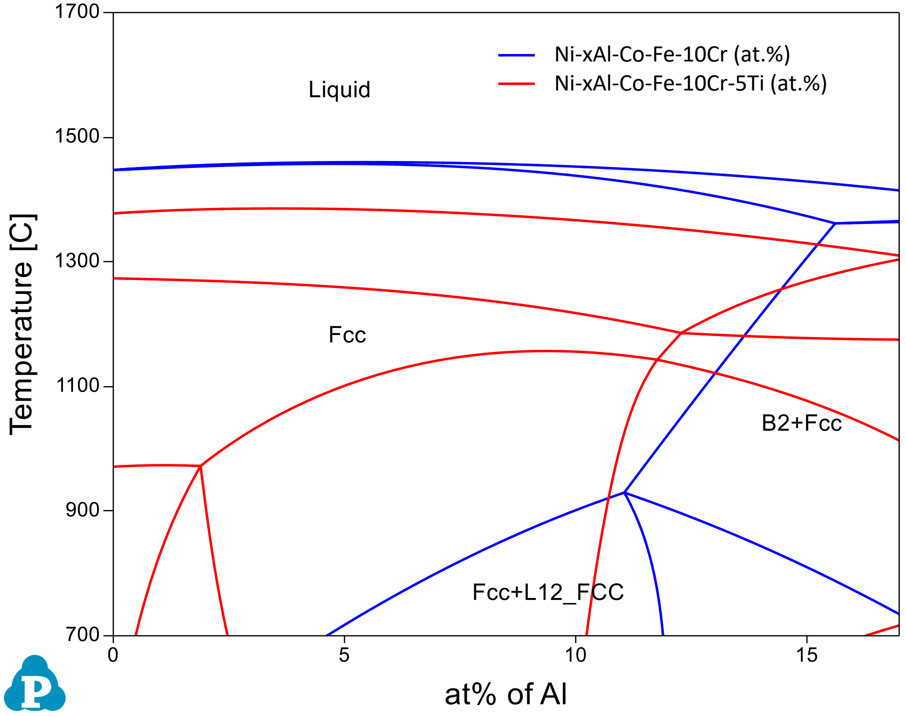


Effect of 5 at% Mn on the isoplethal section of Ni-xAl-Co-Fe-10Cr(at%)

HEA Bond Coats

Ni-Co-Fe-17Al-10Cr-X (at%)





Effect of 5 at% Si on the isoplethal section of Ni-xAl-Co-10Cr-Fe (at%)

Effect of 5 at% Ti on the isoplethal section of Ni-xAl-Co-10Cr-Fe (at%)

HEA Bond Coats

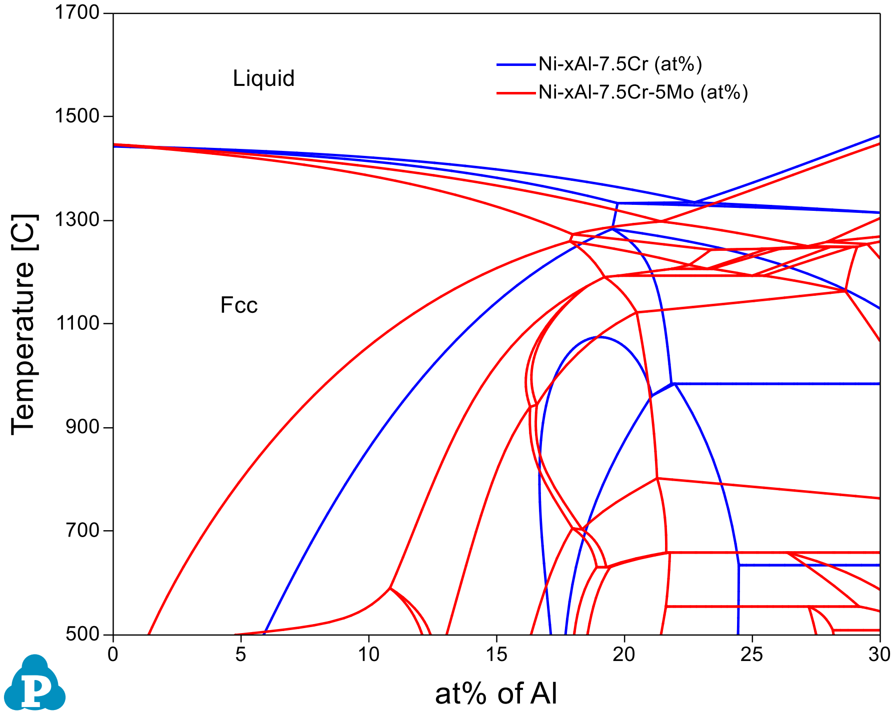
- Isopleths of Ni-xAl-7.5Cr (at%) with and without Mo were explored to investigate its effect the melting temperature and the stability of Fcc phase.

- Mo will decrease the melting temperature of the base alloy.

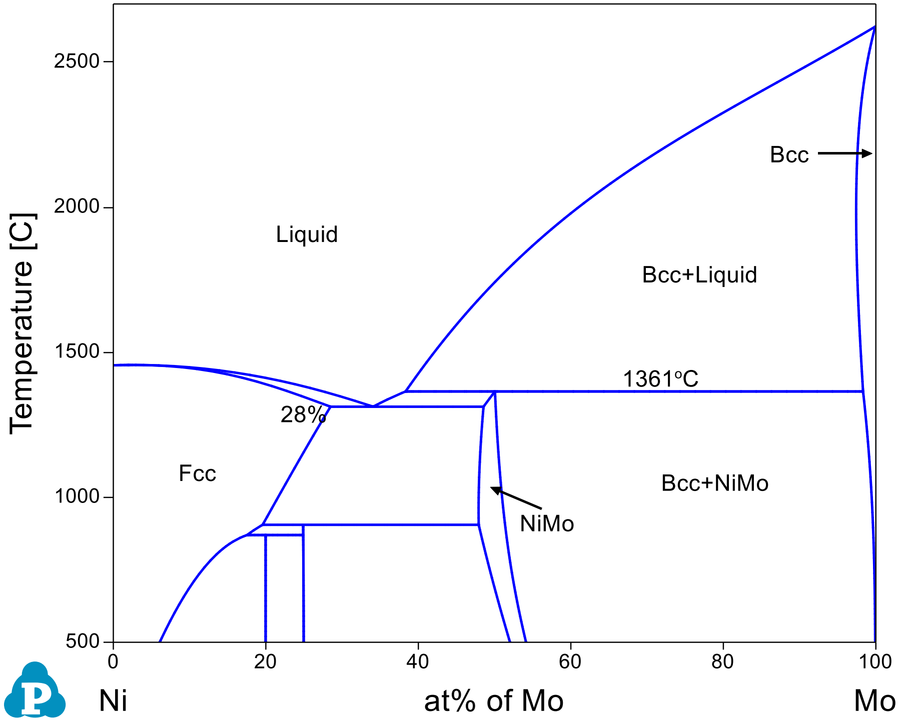
- This can be explained by the Ni-Mo binary phase diagram. Adding a small percent (less than 28 at%) of Mo to Ni will form Fcc solid solution, and the melting temperature will decrease from that of pure Fcc Ni.

- Adding higher Mo to Ni will form an intermetallic phase, and the melting temperature is limited to the three phase equilibrium at 1361°C. The high melting temperature region is only restricted to the small Bcc region.

HEA Bond Coats



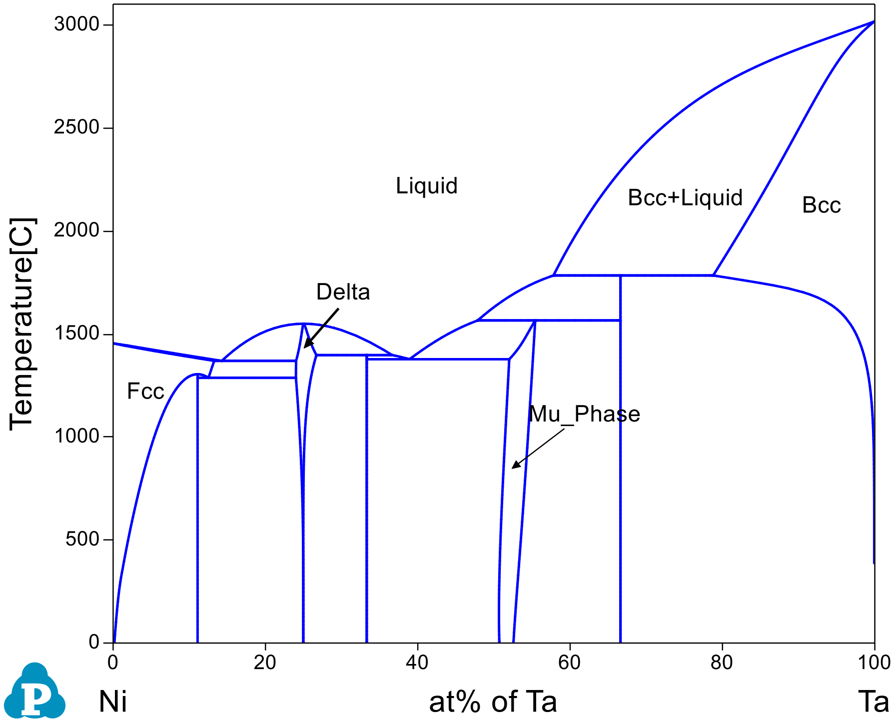
Effect of 5 at% Mo on the isopleths of Ni-xAl-7.5Cr (at%)



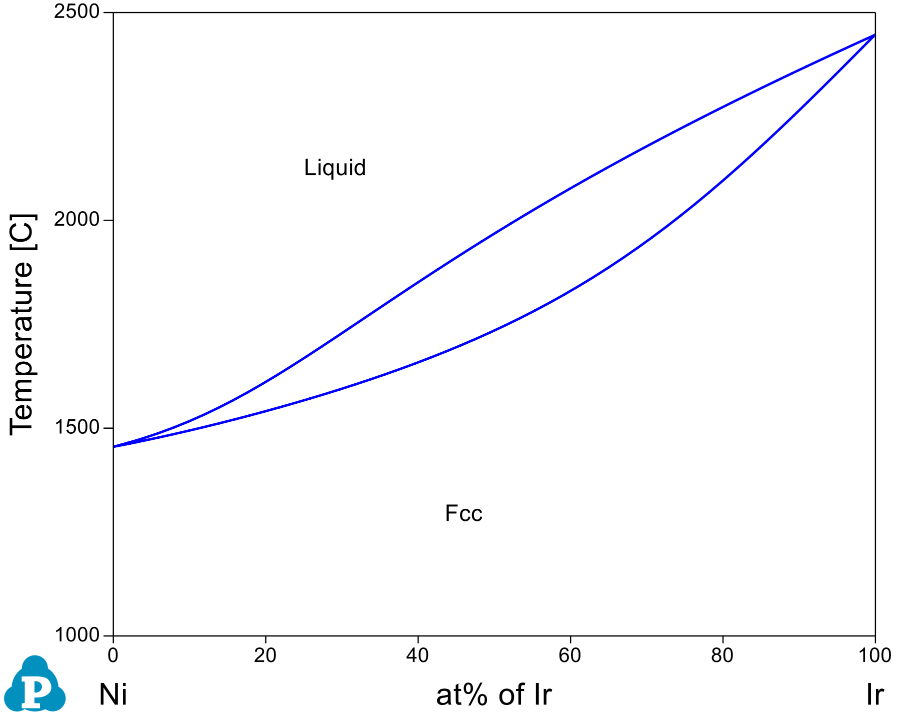
Ni-Mo binary phase diagram

HEA Bond Coats

Ni-X Binary Phase Diagrams



Ni-Ta binary phase diagram



Ni-Ir binary phase diagram

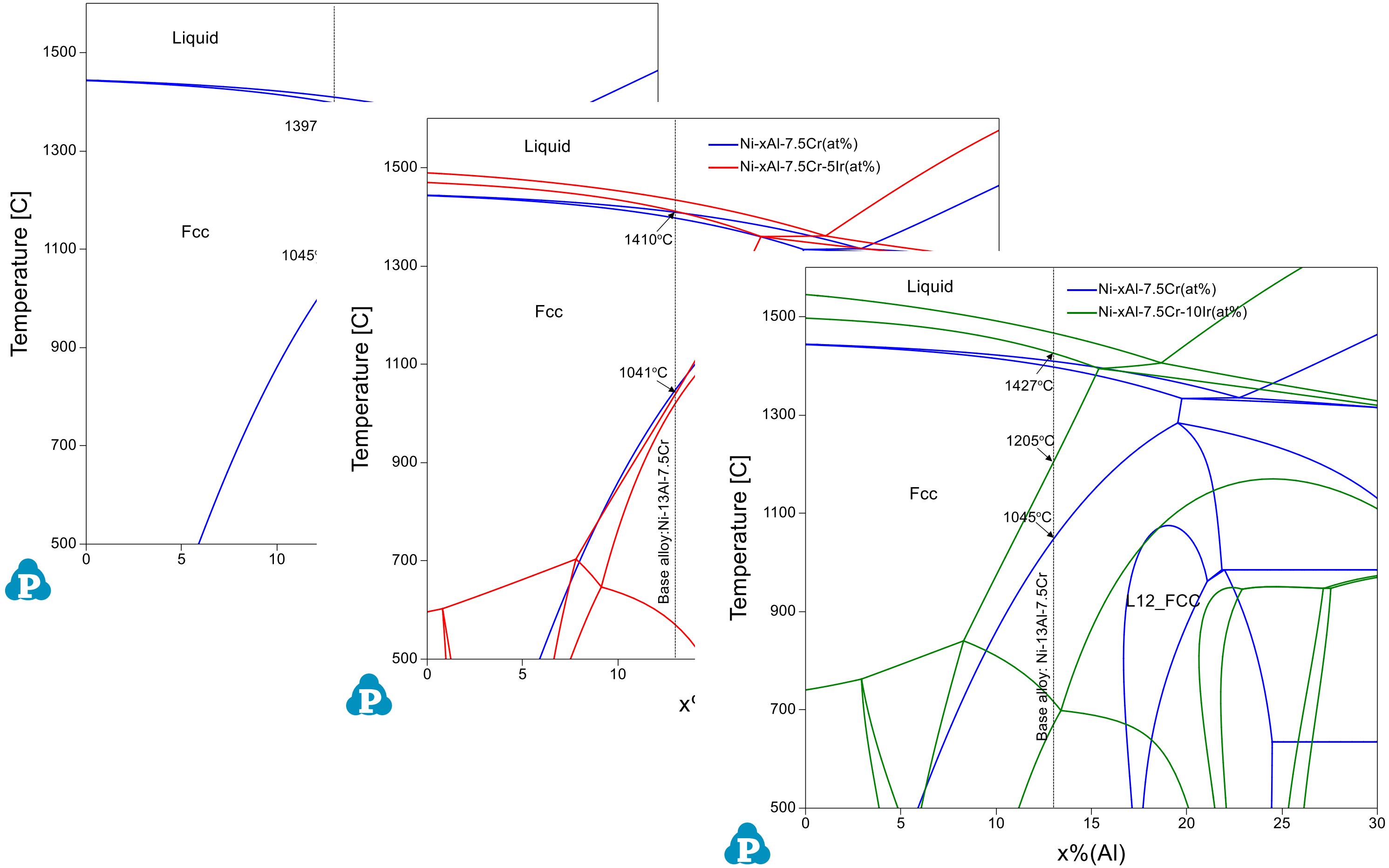
HEA Bond Coats

For the Ni-13Al-7.5Cr (at%) based alloy, Ni is the major component. To search for the elements that may have positive effect on the melting temperature, we have performed calculations for many Ni-X binary systems. A few elements are identified to have the potential to enhance the melting temperature of the base alloy. The following conclusions were obtained:

- Ir and Rh increase the melting temperature of Ni by ~4^{o}C/at%, and increase the stability of Fcc;
- More than 20 at% of Pt is needed to increase the melting temperature of Ni;
- Small amount of Re and Ru help increasing the melting temperature of Ni, but high percent of these two elements are no good.

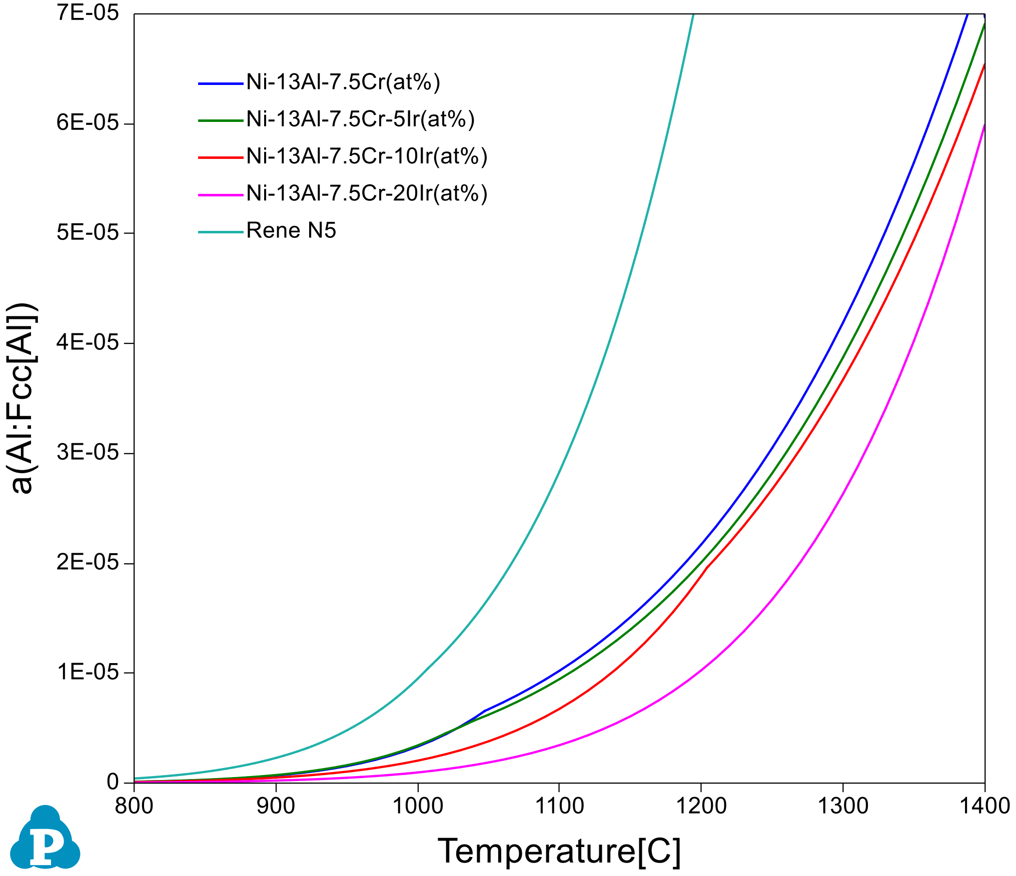
HEA Bond Coats

Ni-xAl – 7.5 Cr + Ir



CompuTherm
FOR MATERIALS DESIGN

Chemical Activity Matching



Effects of Ir on the activity of Al based on a Ni-13Al-7.5Cr (at%) alloy

CompuTherm FOR MATERIALS DESIGN

Directed Vapor Technologies International, Inc.

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.