Multi-Component/Multi-Phase Alloys as Precursors to Protective/Functional Surfaces via Gas Reactions

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What is this Talk About?

- **Formation of <u>Near-Surface</u> Structures by Oxidation**
  - -Potential Applications < Than 10 Microns Thick
  - -Oxidation Reaction of the Surfaces of Bulk Alloy Components or Deposited Alloy Films
  - -Not a Talk on Synthesis of Bulk Ceramics

- **Manipulation of Alloy Metallurgy to Control the Surface Oxidation Products that are Formed**
  - -Identification of Oxidation Phenomena That Can be Used to Make Protective/Functional Surfaces
  - -Focused on **Nitride** and **Carbide** Formation

Motivation for this Work is to Explore Extension of Oxidation Alloy Design Principles to the Emerging Functional and "Nano" Areas of Research

Three Concepts Will be Forwarded for Consideration

- **External, Continuous Protective Nitride, Carbide, etc Scale Formation via Selective Oxidation**
  -primarily simple (binary) phases: e.g. TiN

- **Use of <u>Intermetallic Compounds</u> as <u>Precursor Structures</u> to Form Complex (Ternary^{+}) Nitride, Carbide, etc. Phases by Oxidation (Internal and External)**

Linked

- **Use of <u>Multi-Phase</u> Alloy Microstructures as a <u>Template</u> to Controllably Yield Composite Surface Structures via In-Place Internal Oxidation**

A Series of Phenomenological Examples Will be Presented in Support of These Concepts

- The “Science” of this Talk is in the Identification of Oxidation Phenomena/Attempts to Control of These Patterns of Behavior to Make Functional Surfaces

- The Specific Motivation/Technical Utility for Each System will be Described
  - -Some “why’s” more developed than others
  - -Talk will become progressively more speculative

Formation of Protective Nitride Layers by Selective Oxidation

Why Would You Want to Form a Protective Nitride Layer?

•Many Nitrides (Carbides, Borides) are **Electrically Conductive** and **Corrosion Resistant**

•Of Interest for Fuel Cell and Battery Applications

•Protective Nitride Layer on Metallic Bipolar Plates in Proton Exchange Membrane Fuel Cells (PEMFCs)

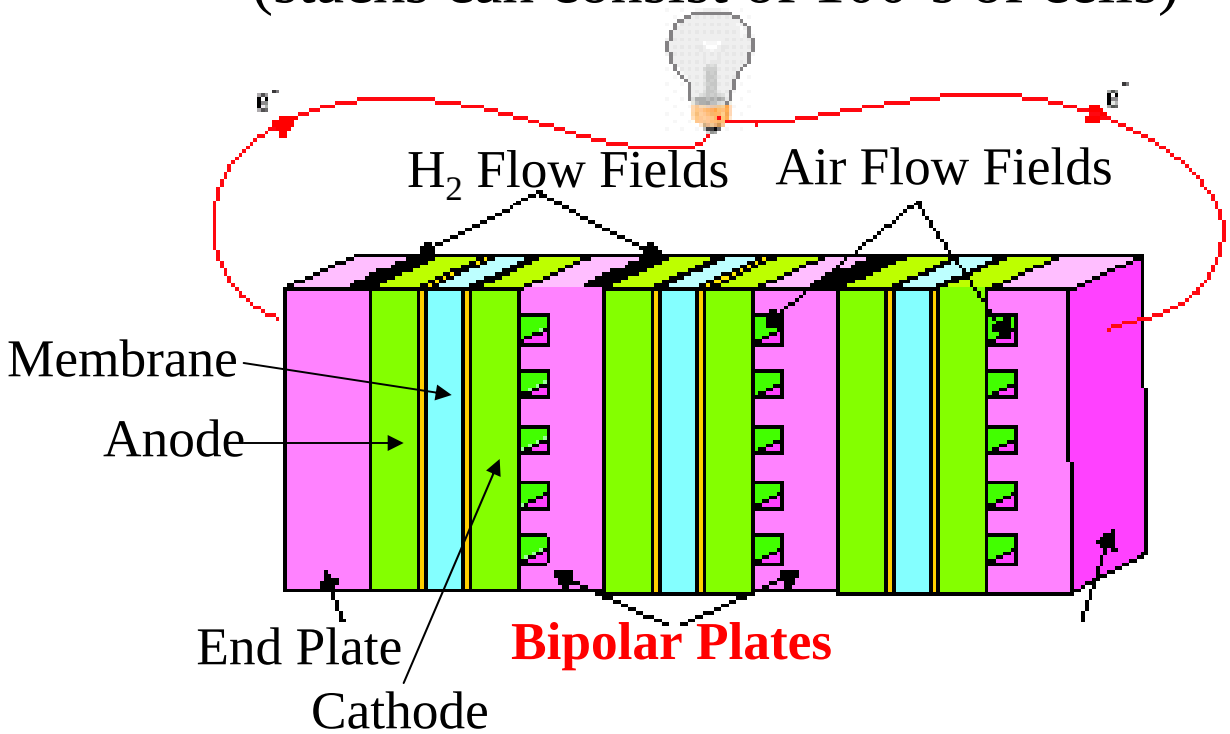
-These are l**ow-temperature** (60-90°C) fuel cells

-Acidic Environment

Bipolar Plates Connect Individual Fuel Cells in a Stack and Separate/Distribute H_2/O_2 Gases

3-Cell Portion of a PEM Fuel Cell Stack

(stacks can consist of 100's of cells)



- Connects anode of one cell to cathode of next, hence "bipolar"
- Same function as interconnect component in solid oxide fuel cells

Thin Metallic Bipolar Plates for Manufacturability and High Power Density

- Replacement for Currently Used Graphite Plates
  - -Brittle: thick (low stack power density), expensive to machine

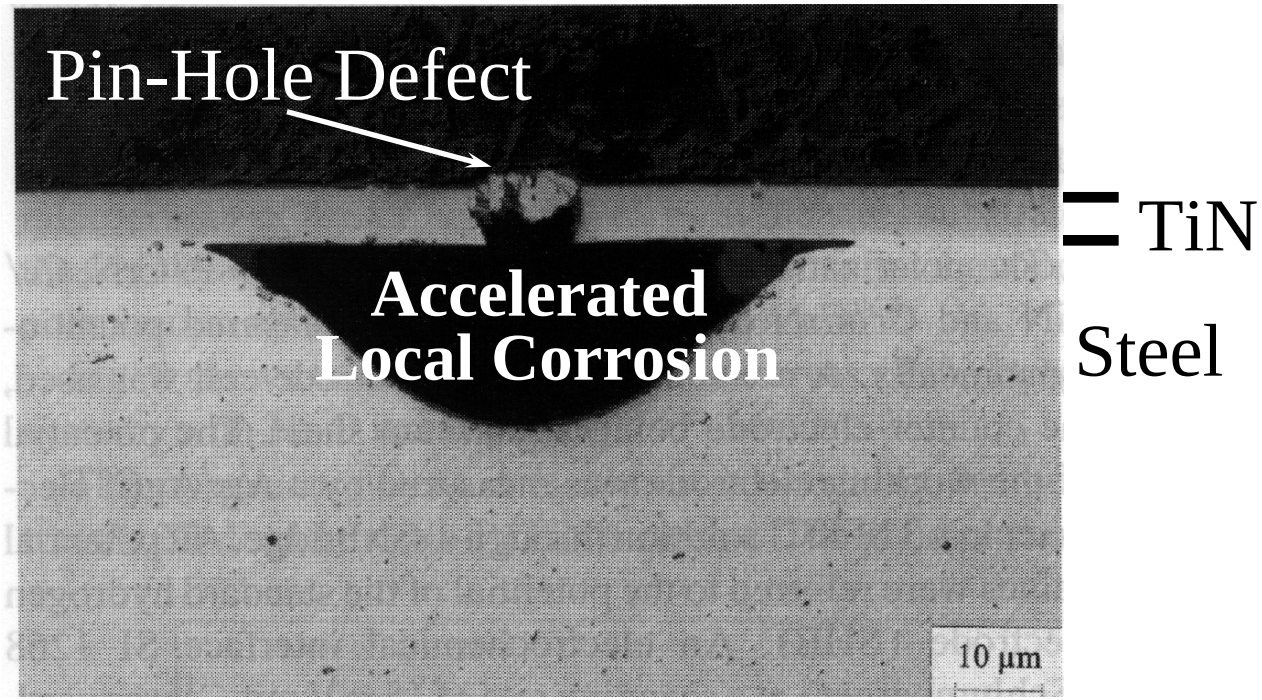
- Problem: Metals Corrode in Acidic Fuel Cell Environment
  - -Cathode side: oxides that form increase contact resistance
  - -Anode side: metal ion dissolution contaminates membrane
  - -Stack performance degraded

- Nitrides are Candidate Protective Coatings for Metal Bipolar Plates
  - **-Our Goal is to Form a Protective Nitride Coating by Selective Oxidation**

Why Not Just Deposit a Nitride Coating?

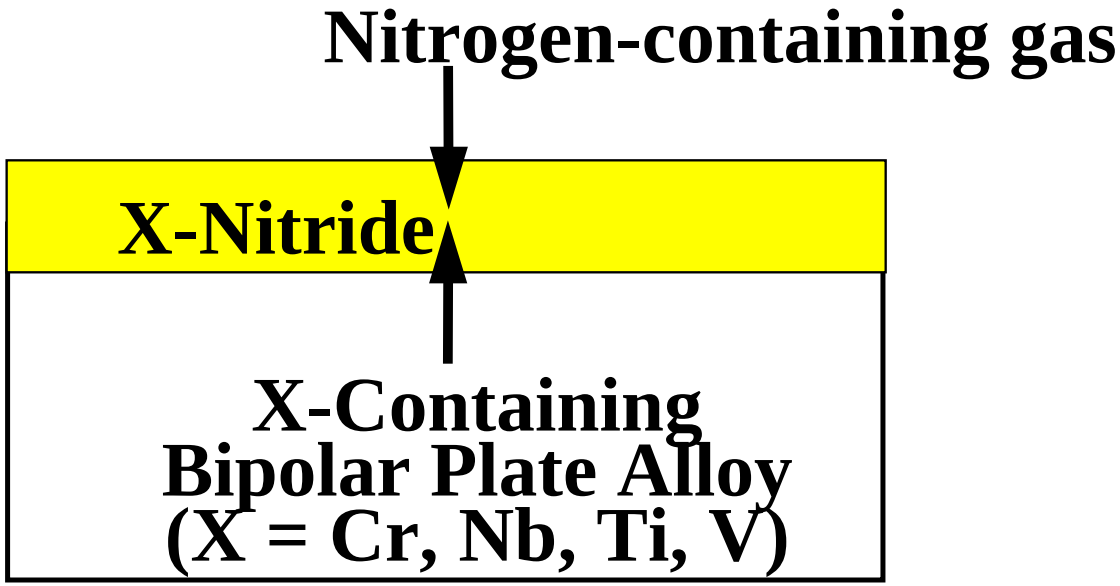
Deposited Coating Methods Typically Leave Pin-Hole Defects

Accelerated Local Corrosion in TiN Coated Steel
(Brandl and Gendig,1996)



- Pin-holes result in unacceptable corrosion resistance
  - -ppm levels of metal ions can degrade polymer membrane
- Good coverage of bipolar plate flow field grooves also difficult

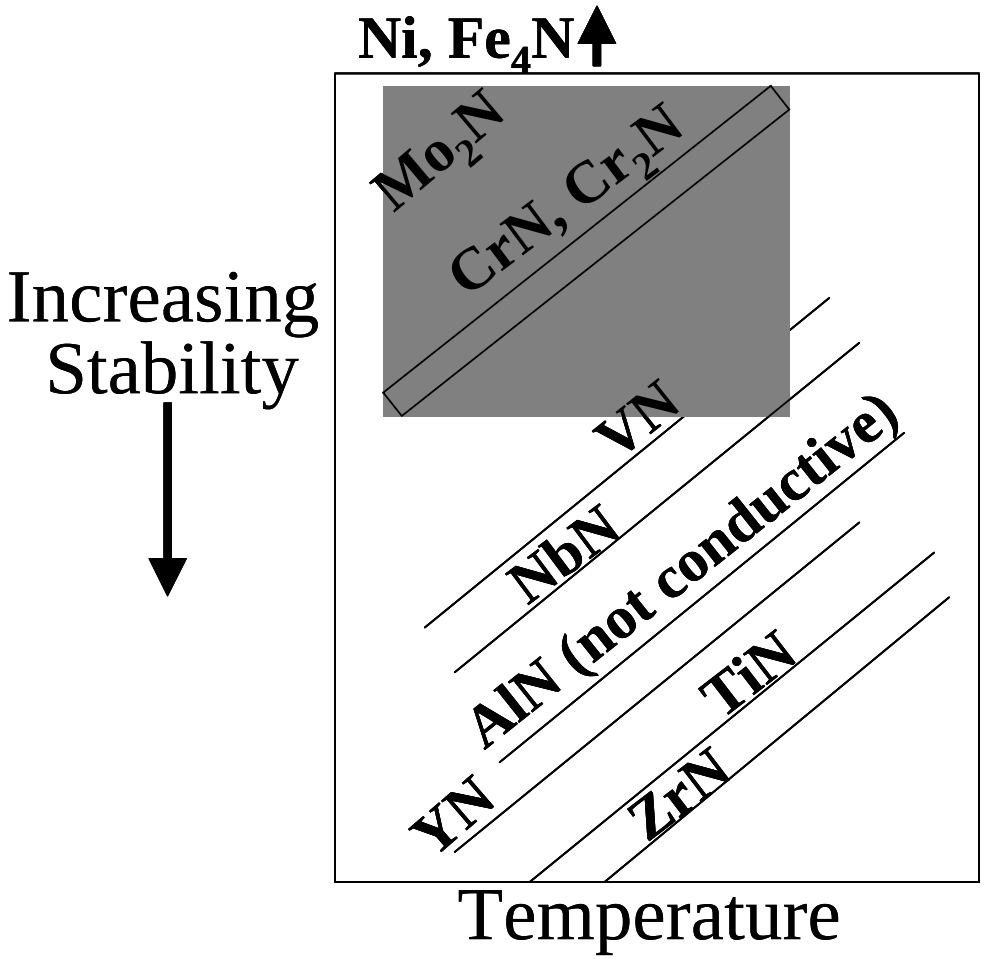
Selective Oxidation to Yield Dense, Pin-Hole Free Coatings



- High Temperature Oxidation Favors Reaction of All Exposed Metal Surfaces
  - -No pin-hole defects
  - -Amenable to grooves/edges (not line of sight limited)
- Challenge is Getting External Scale of Desired Composition to Form and Remain Adherent on Cooling
  - **-This is what our community does!**

Nitride Formation on Ni- and Fe- Base Alloys

Schematic Ellingham Diagram for Nitridation

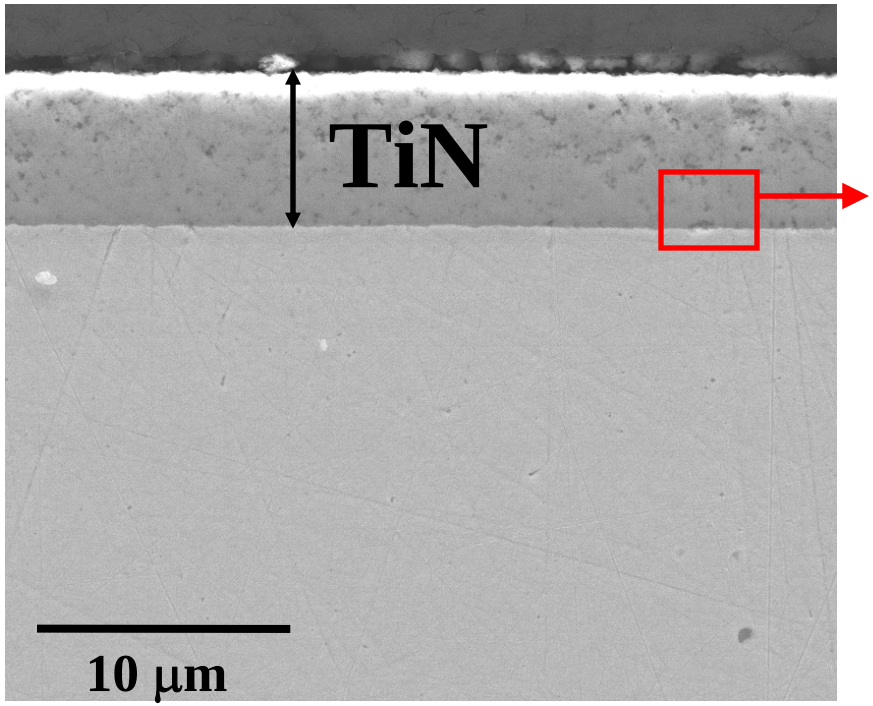


- Nitride-forming additions of Cr, Nb, Ti, V, Zr to Ni/Fe
- Nitridation from 800-1200°C in N_2 and N_2-4H_2

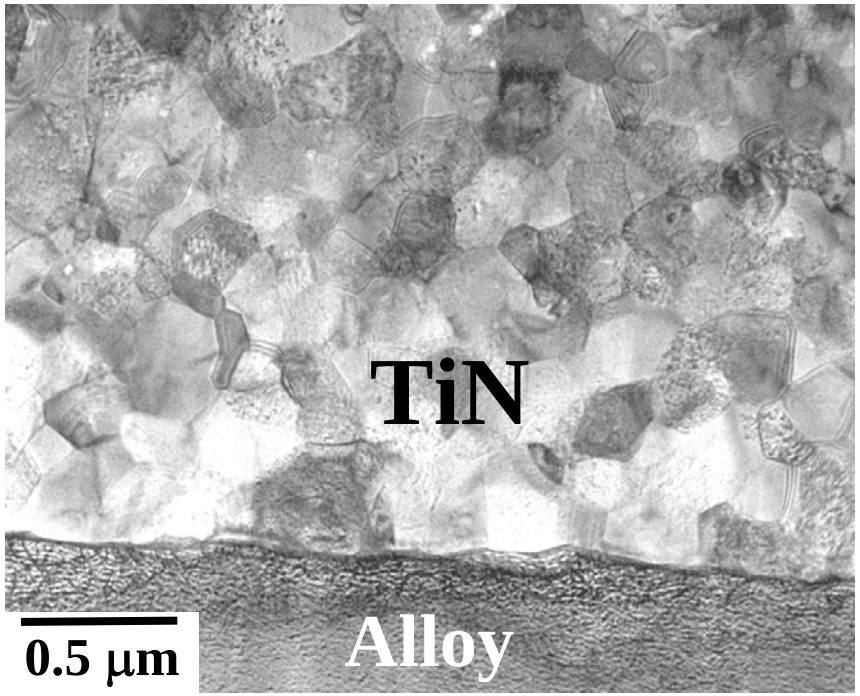
Continuous TiN Formed on Nitrided Ni-12Ti

Ni-12Ti At.%, 1100°C, 48 h, N_2

SEM



TEM

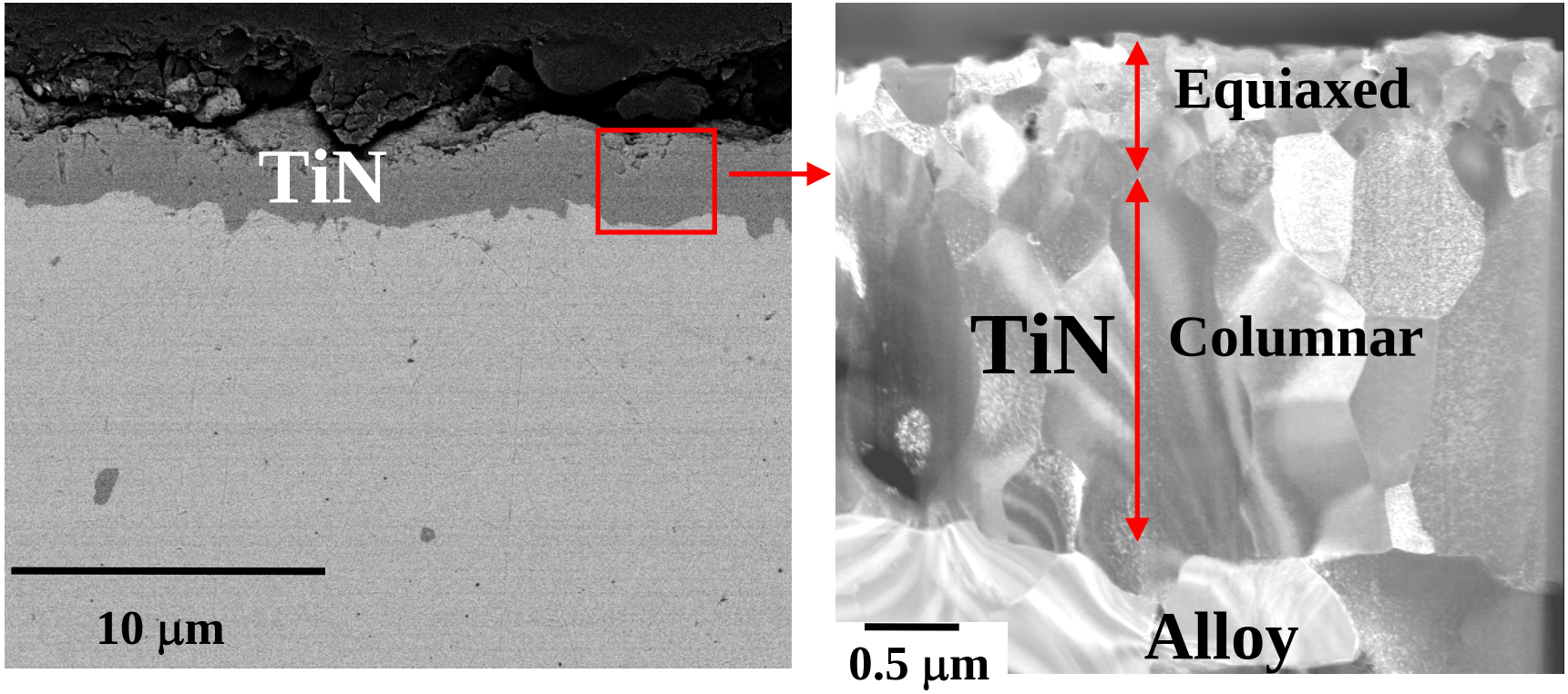


- Equiaxed TiN: 0.1 – 0.3 μm grain size and ~ (45-50) at.% N
- Transition to external TiN at Ni-(1-2.5) at.% Ti at 1020°C (Savva et al., 1996)

TiN Also Readily Formed on Fe-17Ti At.%

Fe-17 Ti At. %, 1100°C, 36 h, N_2

SEM **STEM**

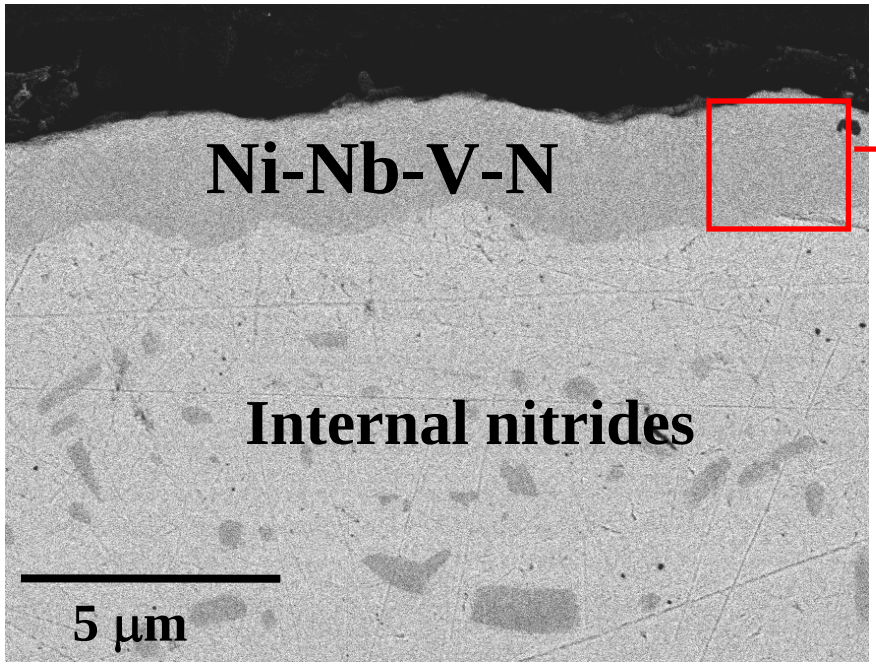


- Transition from equiaxed to columnar TiN (~50 at.% N)
- External TiN at ~ Fe-(6-10)Ti (2-phase alloy with $TiFe_2$)

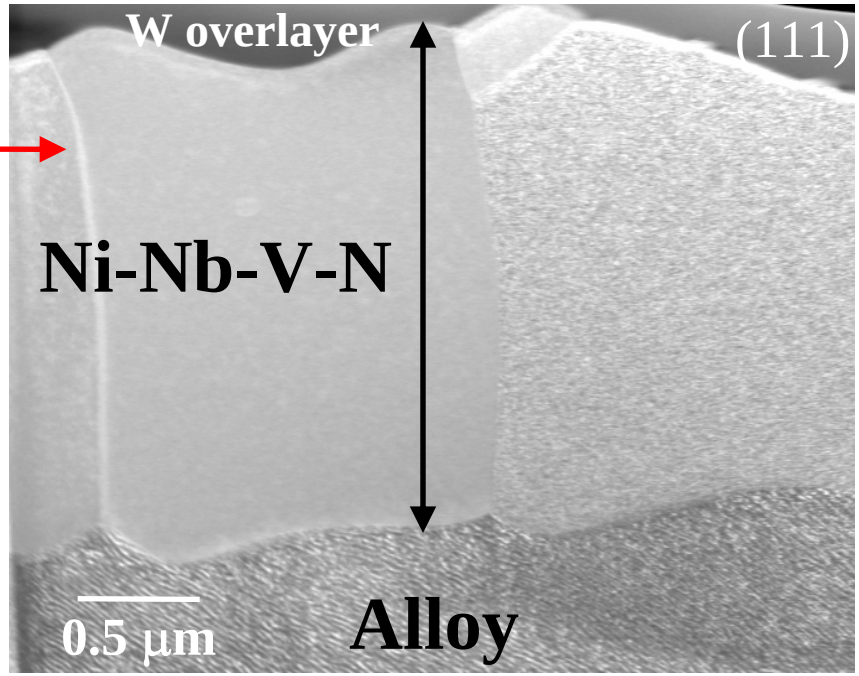
Complex Nitride Formation Also Possible

Ni-6.5Nb-6V At.%, 1100°C, 24 h, N_2

SEM



STEM

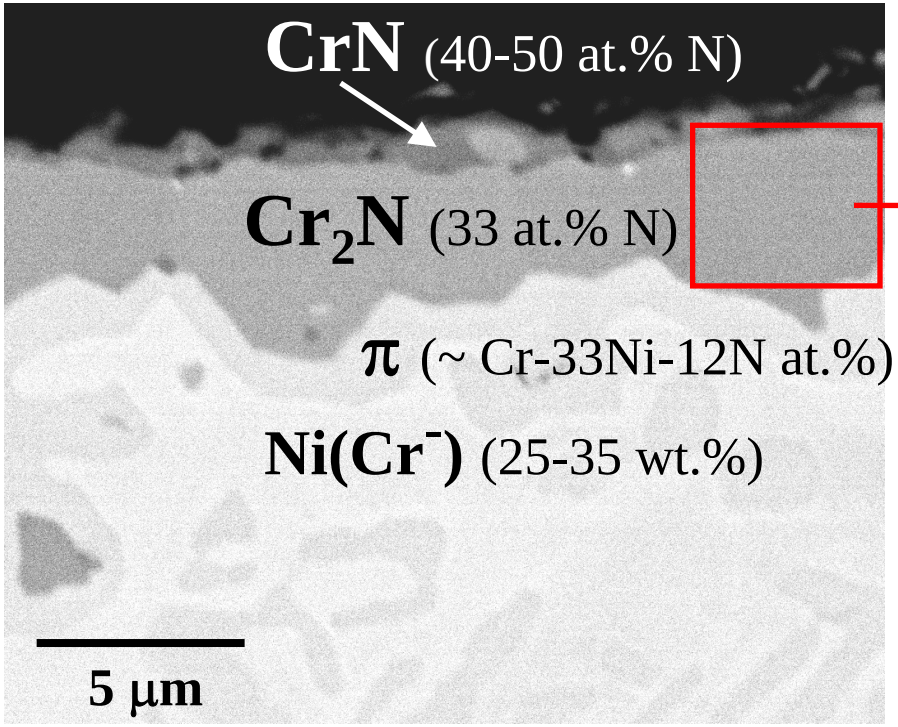


- Attempted to increase reactivity of Ni-6.5Nb by V addition
- Complex nitride directly formed (likely a solid solution)
  - -Scale composition: Ni-(12-15)V-(15-20)Nb-(20-30)N at.%
  - -Ni matrix and Ni-Nb-V-N both FCC ($Fm\bar{3}m$)
  - -Parent/product similarities can favor complex phase formation

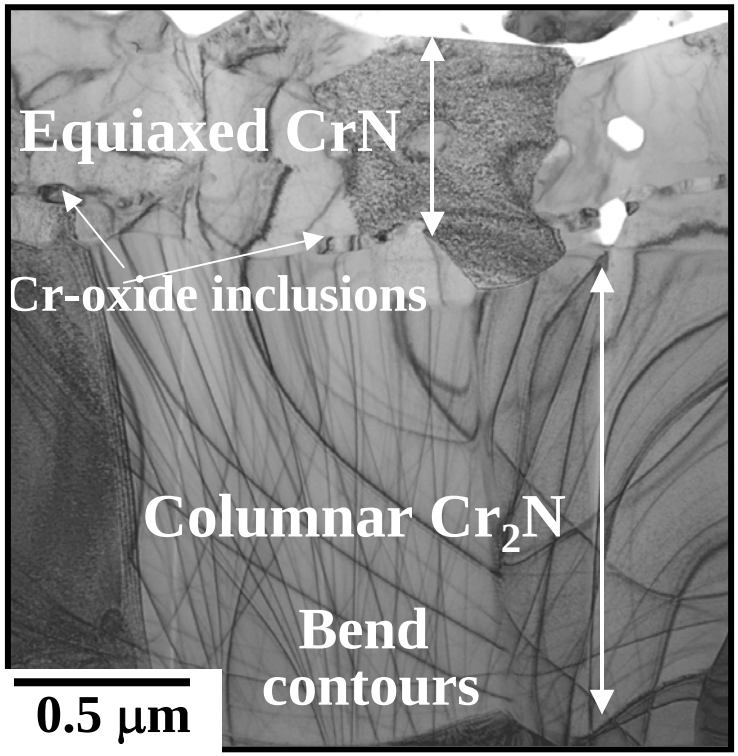
Best Success for Fuel Cell with CrN/Cr_2N Surfaces on ~Ni-(33-55)Cr At.%

Ni-53Cr At.%, 1100°C, 2 h, N_2

SEM

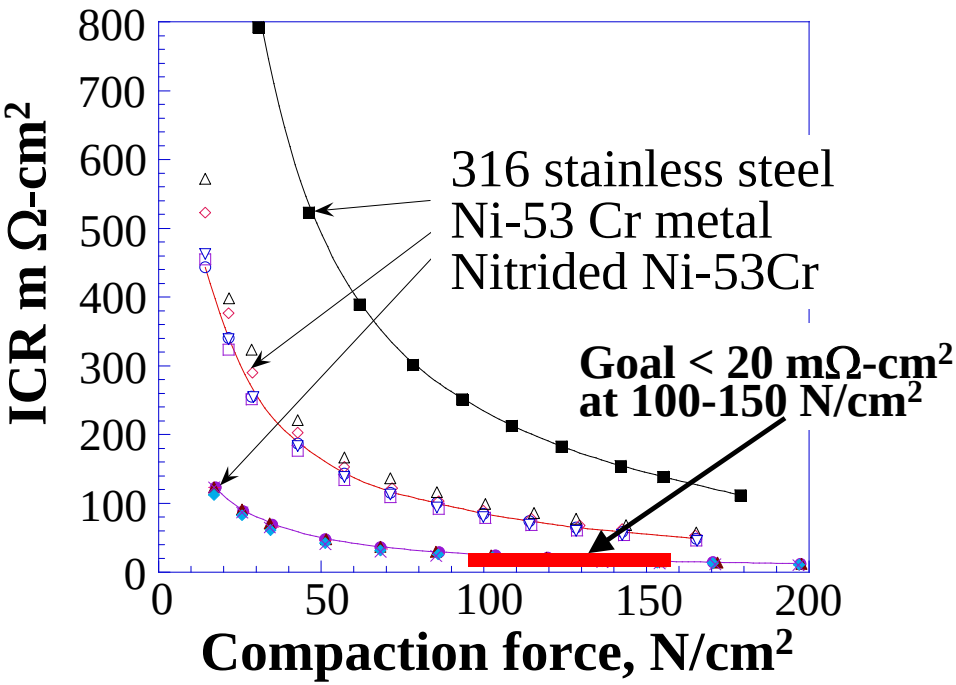


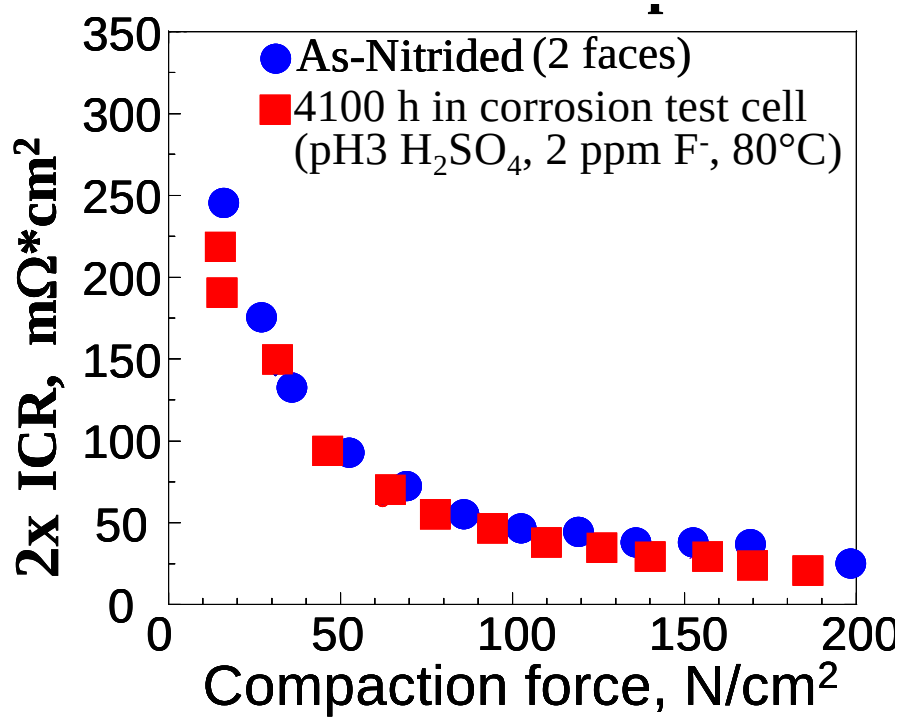
STEM



- Need ~33-44 Cr at.% Cr for external CrN at 900°C (10% NH_3)
  - -Much higher Cr level than needed for Cr_2O_3 (Rubly and Douglass, 1990)
  - -Increased N_2 permeability with increasing Cr in Ni (Christ et al., 2003)

Nitrided Ni-53Cr Exhibits and Maintains Low Contact Resistance After 4100 h Corrosion Exposure



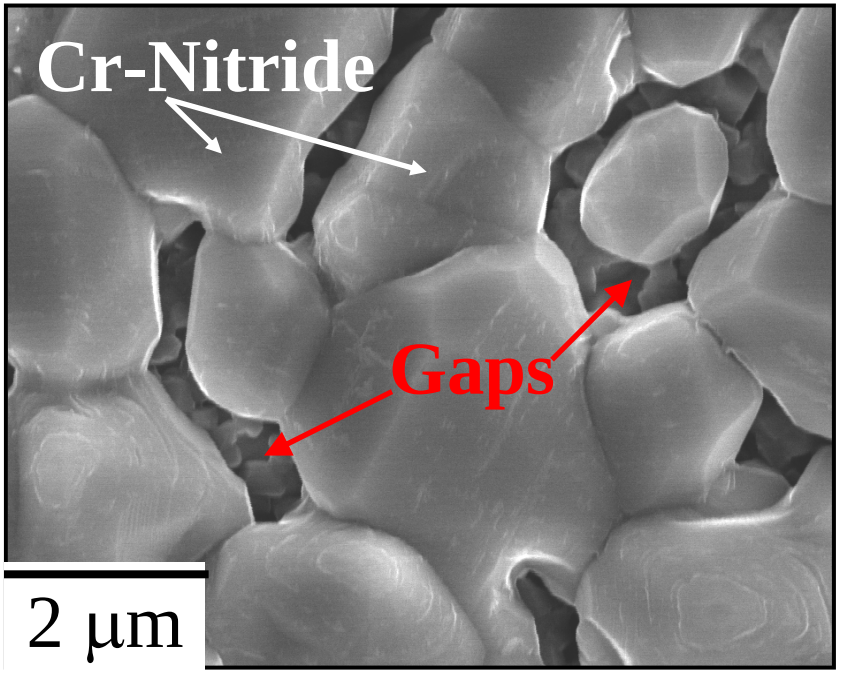


- Successful fuel cell tests at Los Alamos, GM, others

- Proof of principle established that thermally grown Cr-nitrides can protect metallic bipolar plates

Need to Form Protective Cr-Nitride on Fe-(20-30)Cr At.% Alloys to Meet Bipolar Plate Automotive Cost Goals

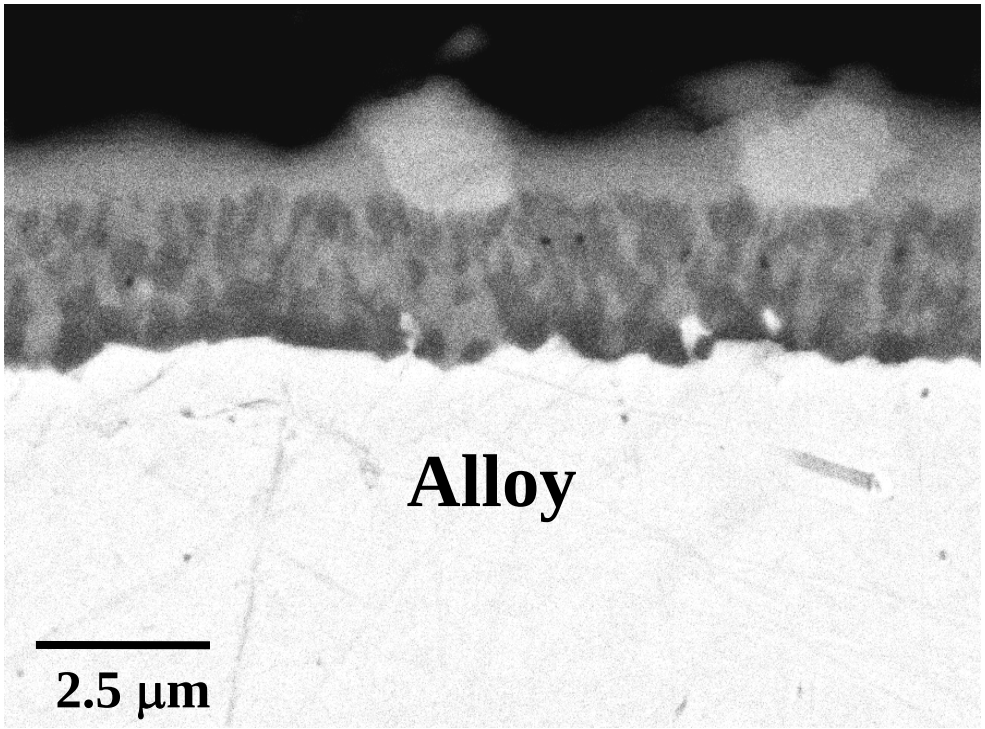
SEM Surface of Fe-28Cr at.%: 1100°C, 2 h, N_2-4H_2



- High N_2 permeability/extensive internal nitridation doesn't allow dense Cr-nitride surface to form
  - -Leaves internally nitrided, Cr-depleted Fe(Cr) unprotected

N_2 Penetration Reduced by Initial Oxide Formation from O_2 Impurities in N_2-$4H_2$ Gas

SEM Cross-Section of Fe-28Cr-6V at.%, 900°C, 24 h, N_2-$4H_2$



Cr_2N (light)

$CrVO_4$ (dark)

- V was added in attempt to modify growth of Cr-nitride
- Dense V-modified Cr_2N formed at surface
  - -promising corrosion/contact resistance results
- Inner mixed oxide indicates important role of oxygen impurities

Protective Layers of Nitride, etc. Scales Can be Formed by Selective Oxidation

- Simple extension of selective oxidation alloy design principles

- Interesting opportunities to study and leverage 3rd element, reactive element effect, etc. analogs with species other than oxygen to form protective layers

- Primarily amenable for simple (binary) phase formation
  - -Niche applications available where a high level of corrosion protection is needed along with conductivity, hardness, etc. other unique properties of nitrides, carbides, …

Complex (Ternary^{+}) Ceramic Phases of More Widespread Interest for Functional Applications

- **Catalytic, Electrical, Magnetic, Optical, etc. Properties**
  -e.g. perovskites (ferroelectrics, superconductors, …)

- **Ternary and higher order gives opportunity to tune properties**

- **Can We Form Complex Phases by Oxidation Reactions?**

Approach: Complex Phases From Oxidation of Intermetallic Compounds

- **Complex Phase Formation by Oxidation Usually Difficult**
  - -Metal species have different oxidation potentials (basis for selective oxidation)
  - -Need to have metals available at the same place/time to grow ternary lattice

- **Take Advantage of Bonding/Structure of Intermetallics**

- **Particularly Amenable to Complex Nitrides and Carbides**
  - -Strong Interstitial Character (N, C not as electronegative as O)
  - -Coey and Sun, 1990: interstitial N introduced by nitriding $Fe_{17}Sm_2$ to form $Fe_{17}Sm_2N_3$ significantly increased Tc and coercivity of interest for magnetic applications

Extensive Discussions with Bob Rapp Gratefully Acknowledged

Complex Nitrides and Carbides Generally Not Well Explored*

- Far fewer known compounds than oxides

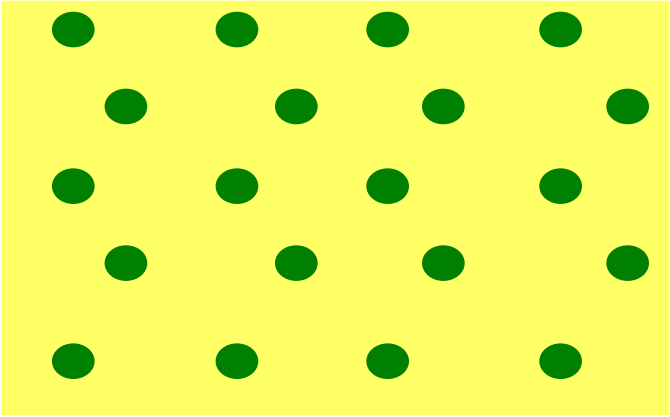
- Complex nitrides/carbides typically made by reaction of complex oxide precursors w/NH_3, CH_4, etc. or by solution chemistry/molecular routes

- Intermetallics offer new set of precursors/chance to form <u>new phases</u> with potentially interesting and useful properties

*exception is nitride semiconductors such as GaN and related phases

Single-Phase Layers Readily Made by Conventional Synthesis Approaches

- **For many functional applications dispersed composite surface arrangements wanted (especially at nanoscale)**
  - difficult to make

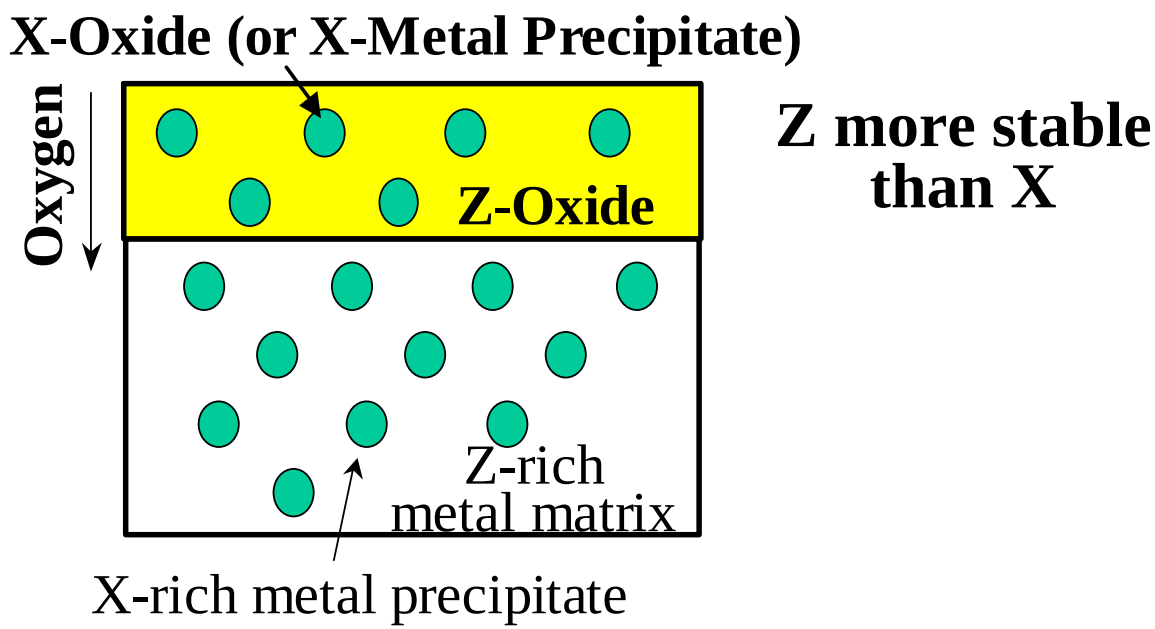


- **Can we form such composite structures by oxidation?**

Internal Oxidation in Two-Phase Alloys To Make Composite Near-Surface Structures

In-Place Mode of Internal Oxidation

(schematic after Gesmundo and Gleeson, 1995)



- Form of internal oxidation unique to multi-phase alloys
  - Spengler,1959; Gesmundo and co-workers, 1990's
- Oxidant inward diffusion >> metal component diffusion
- Phases react **independently**: Yields composite surface which **exactly replicates** initial alloy microstructure

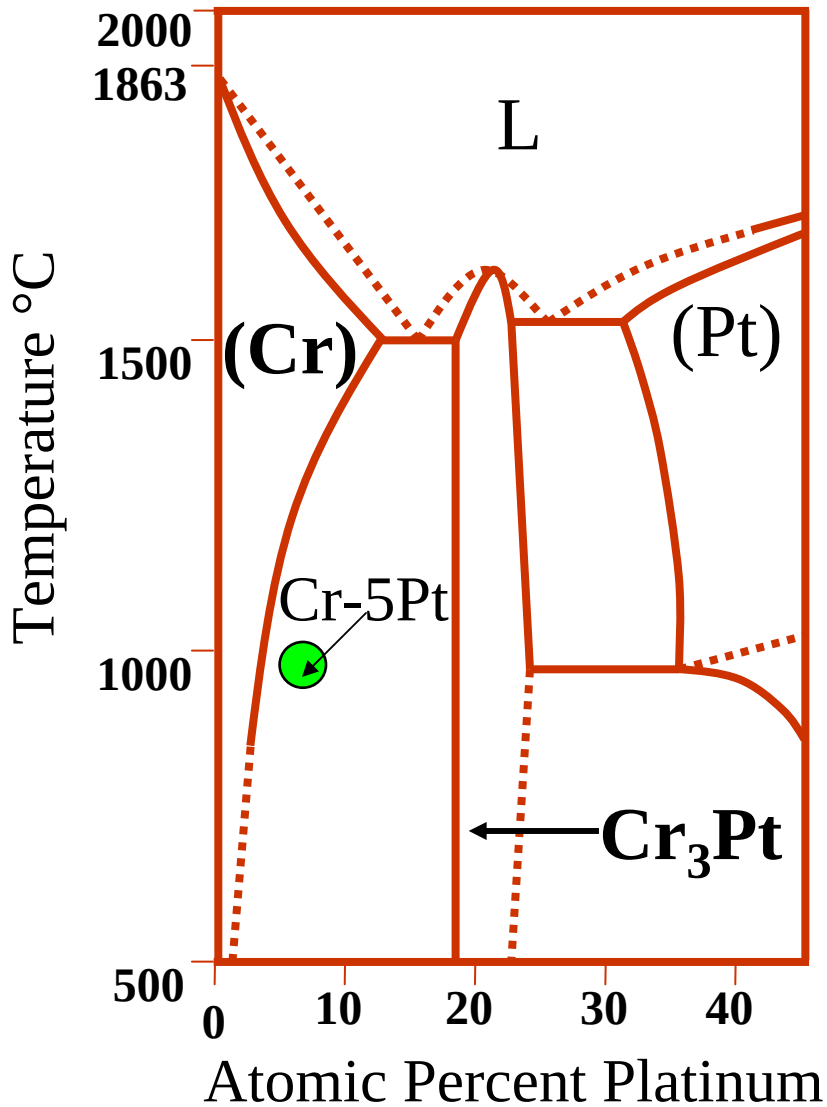
Two Concepts to Form Functional Near-Surface Ceramic Structures by Oxidation

- **Use Initial Two-Phase Alloy Structure as a <u>Template</u> to Control Morphology of Resultant Ceramic Phase(s) via In-Place Internal Oxidation**
  - -Leverage initial alloy phase equilibria to set the template prior to oxidizing

- **Intermetallic Precipitates as Precursors for Complex Ceramic Phase Formation by Oxidation**

Show Microstructural Examples to Illustrate Concepts

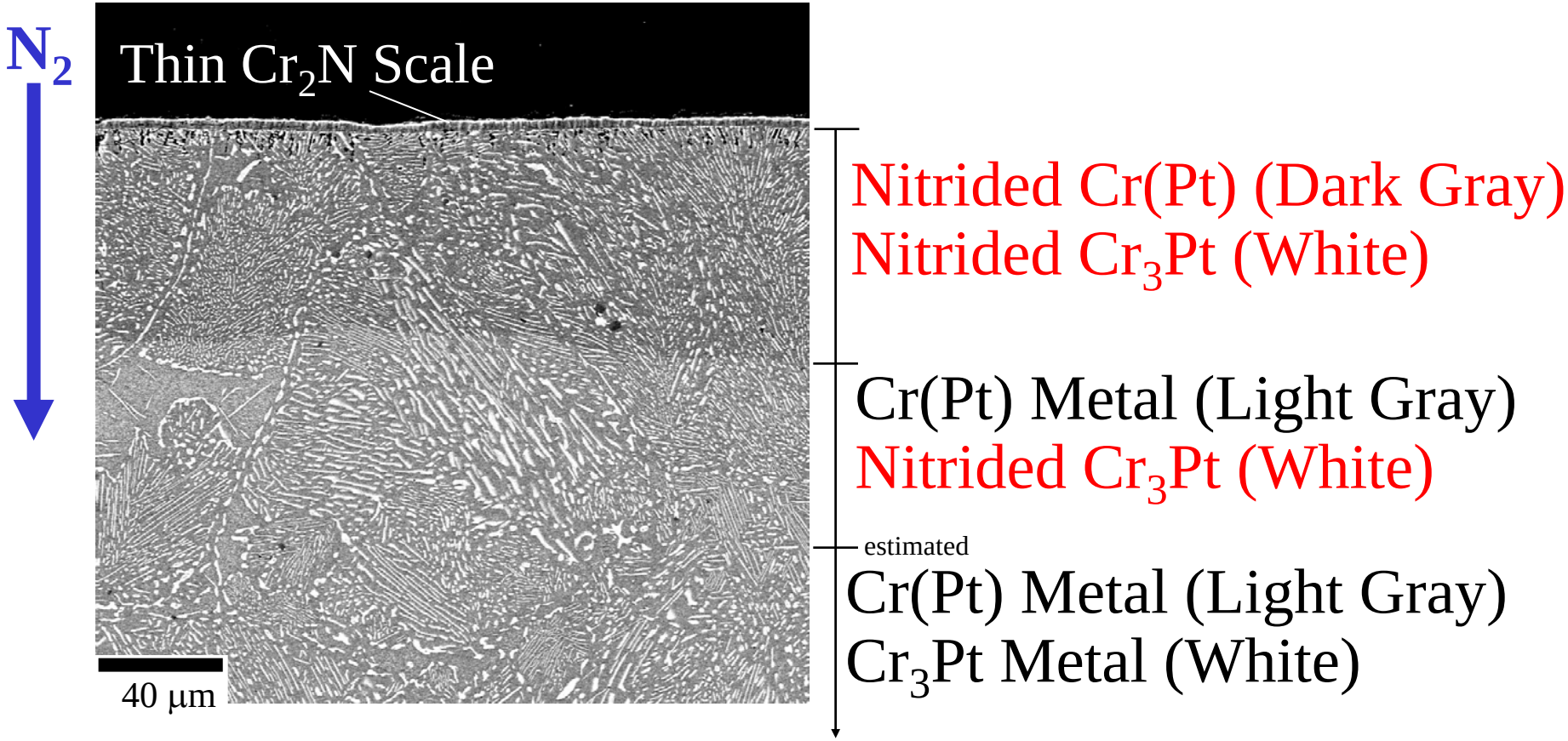
Model System: Can We Form the Ternary Nitride Cr_3PtN at Cr_3Pt Precipitates in Cr?



- Cr matrix exhibits high permeability to nitrogen
- Cr_3Pt second phase can be precipitated
- Cr_3Pt and desired Cr_3PtN have similar metal component stoichiometry
- Cr-5Pt at.% selected for study

Cr-5Pt at.% Exhibited In-Place Internal Nitridation After 24h at 1000ºC in Nitrogen

SEM cross-section micrograph

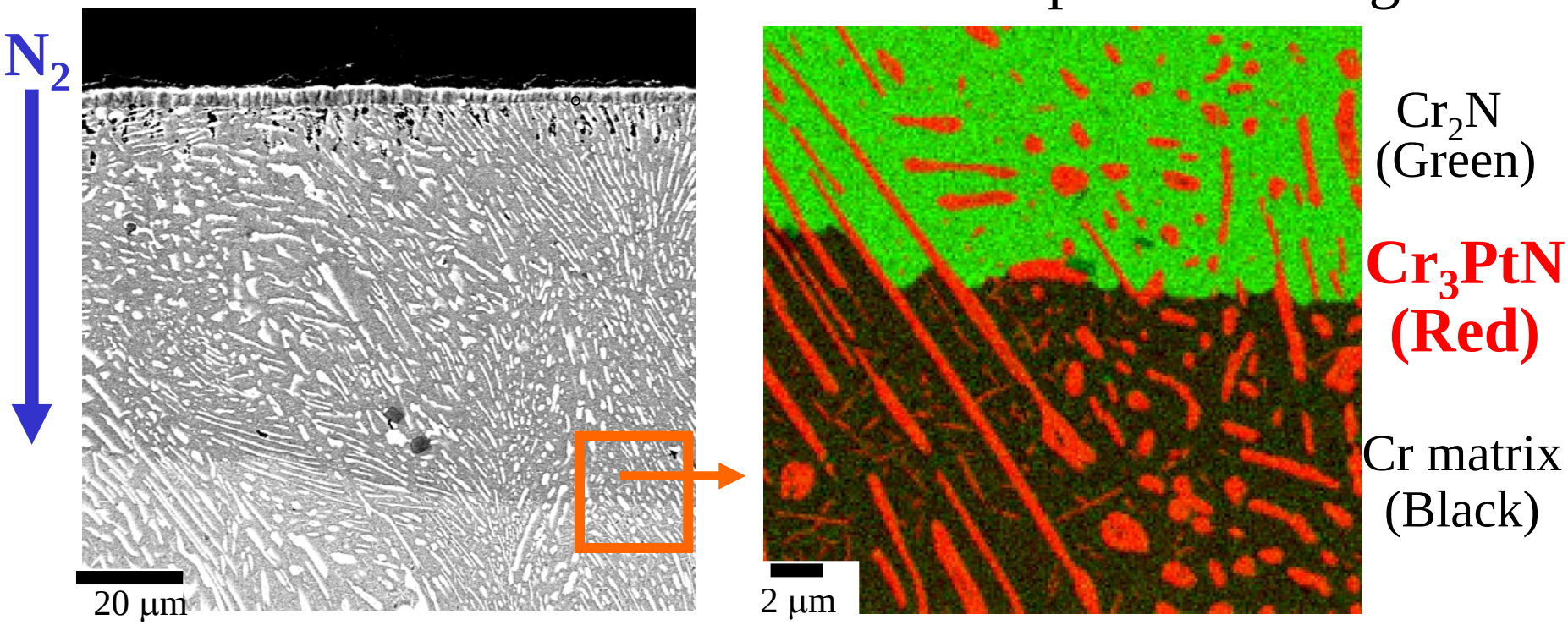


- Reaction exactly followed underlying alloy microstructure
- Cr_3Pt phase nitrided to a greater depth than Cr matrix phase

Microprobe, XRD, TEM Consistent with Cr_3PtN Formation at Cr_3Pt

SEM Cross-Section

LV-EDX Spectrum Image



- Did not form Cr_2N + Pt
- Proof of principle to form complex nitrides at intermetallic precipitates by in-place internal oxidation established
- Control initial alloy precipitation to get desired arrangement then nitride

What are the Mechanistic Details of this Reaction?

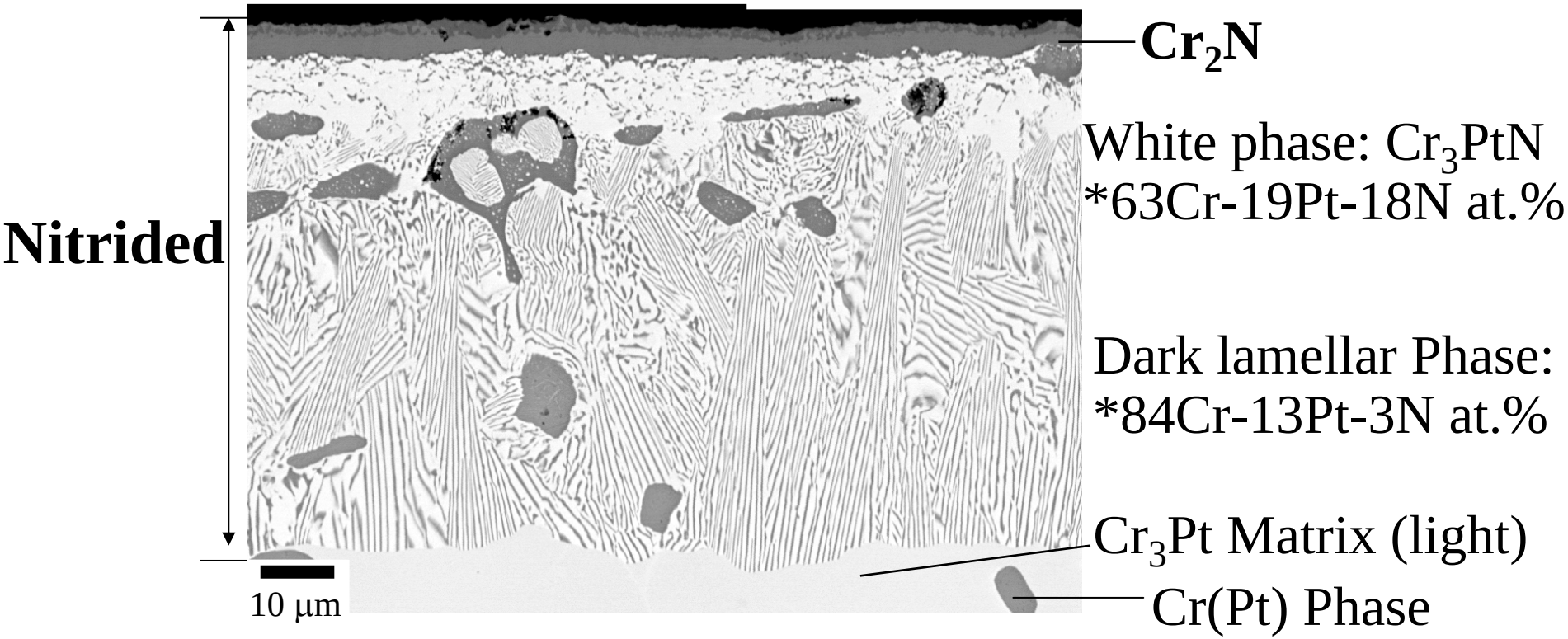
***Gain Insight by Studying the Nitridation of Cr_3Pt and Cr(Pt) Phases Individually and in Combination**

- Single-Phase Cr_3Pt: Cr-17 Pt at. %
- Single-Phase Cr(Pt): Cr-2.25 Pt at. %
- Alloys selected to extend slightly into two-phase field

*S. Wrobel Thesis

Nitrided "Single-Phase" Cr_3Pt Exhibited Cellular-Type Precipitation

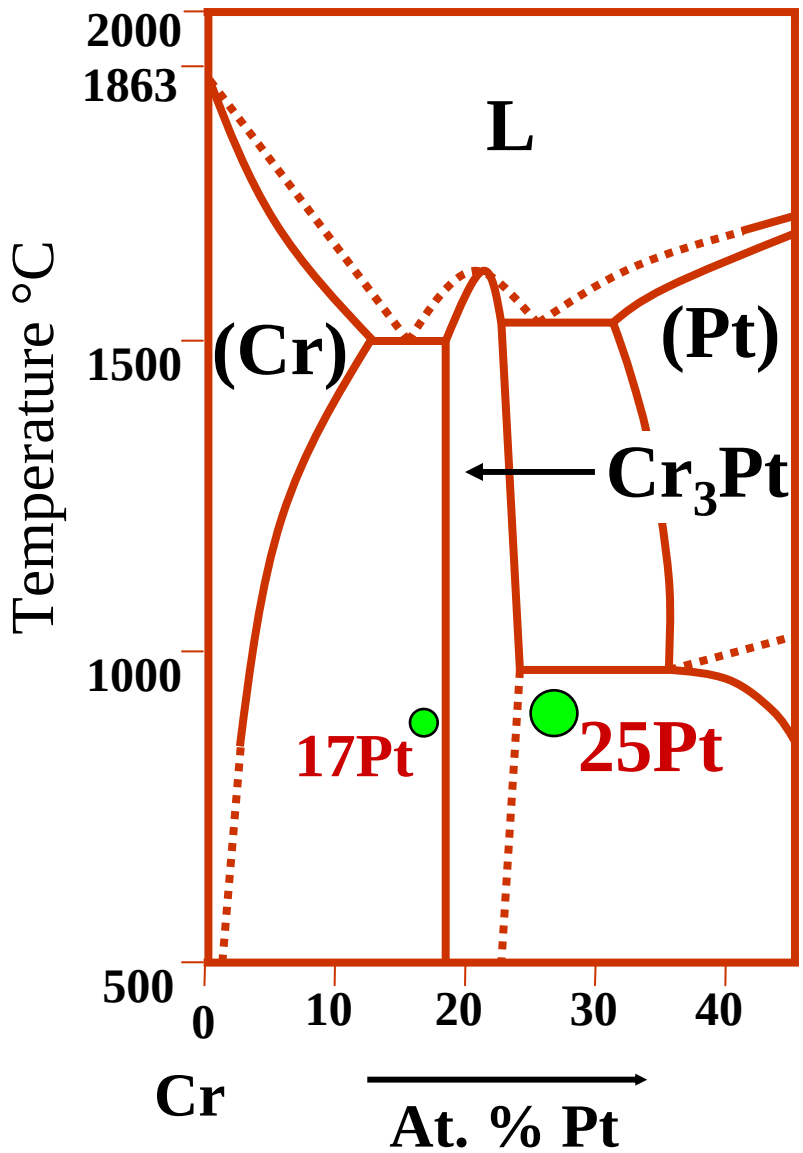
Cross-Section SEM Micrograph of 83Cr-17Pt at.% after 24h at 1000°C in Nitrogen



***Microprobe data semiquantitative due to fine scale**

- Hypothesis: reaction driven by need to eliminate excess Cr to stabilize Cr_3PtN: requires ~3Cr:1Pt
- Cr_3Pt in two-phase Cr(Pt) + Cr_3Pt field Cr-rich- ~ 5Cr:1Pt

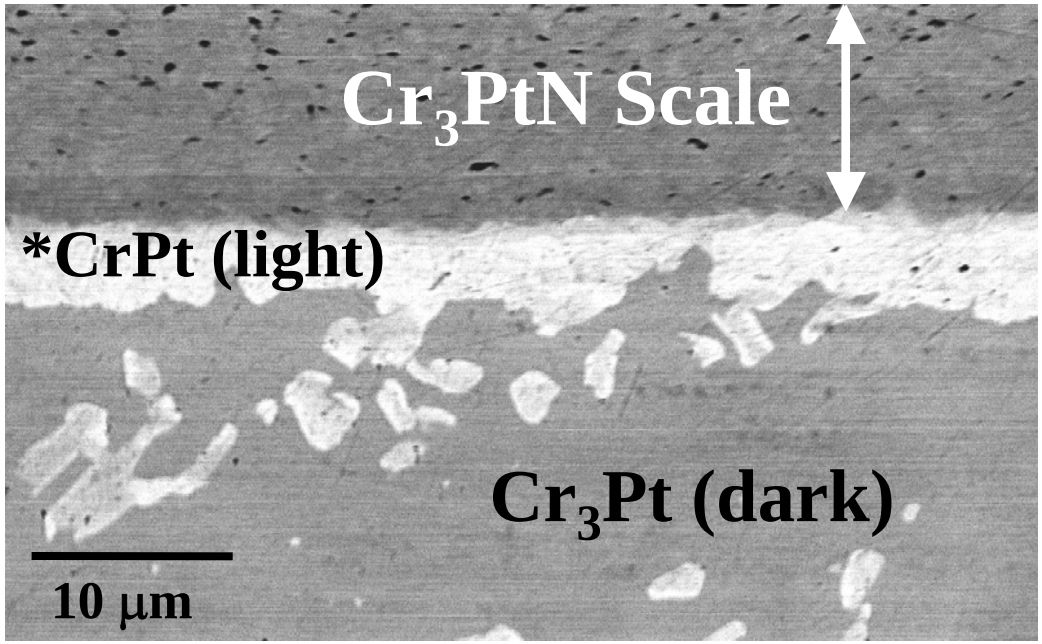
A Cr-Lean Cr_3Pt Alloy with a 3Cr:1Pt was Selected to Test This Hypothesis



- Cr_3PtN requires 3Cr:1Pt
- 75Cr-25Pt at.% Cr-lean Cr_3Pt alloy was fabricated
- Heat-treated at 950ºC for 24 hours to set Cr_3Pt structure

Nitridation of 75Cr-25Pt Cr_3Pt Alloy Yields Single-Phase Cr_3PtN Scale

Cross-Section SEM Micrograph of 75Cr-25Pt at.% after 24 h at 950°C in Nitrogen



- Direct ternary scaling/no cellular precipitation observed
  - -consistent with proposed mechanism
  - -composition ~65Cr-20Pt-15N at.%

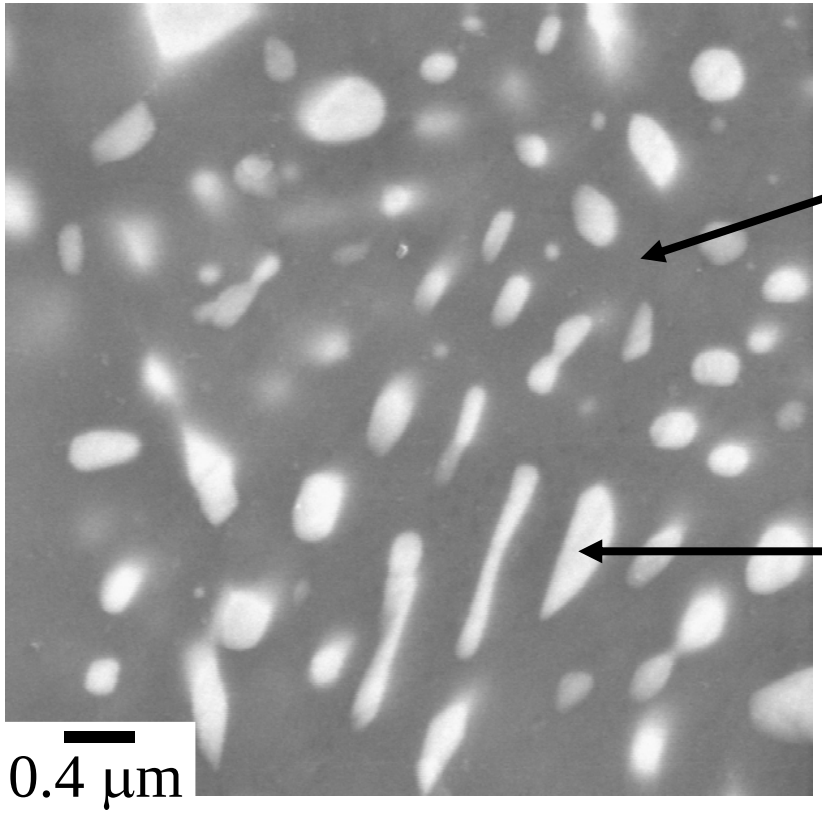
*phase i.d. based solely on composition (65Cr-35Pt at.%)

Why was "Single-Phase" Cr_3PtN formed at Cr-Rich Cr_3Pt Phase in 95Cr-5Pt?

Mechanism further probed by use of single-crystal precursor alloys to alter Cr(Pt) + Cr_3Pt microstructure (collaboration with T.A. Lograsso, Ames Lab)

Fine Cr_3Pt Dispersions Generally Nitride to Form Single-Phase Cr_3PtN

SEM Cross-Section of (111) Oriented Cr-5Pt at.% Single Crystal Nitrided at 1000°C for 24h

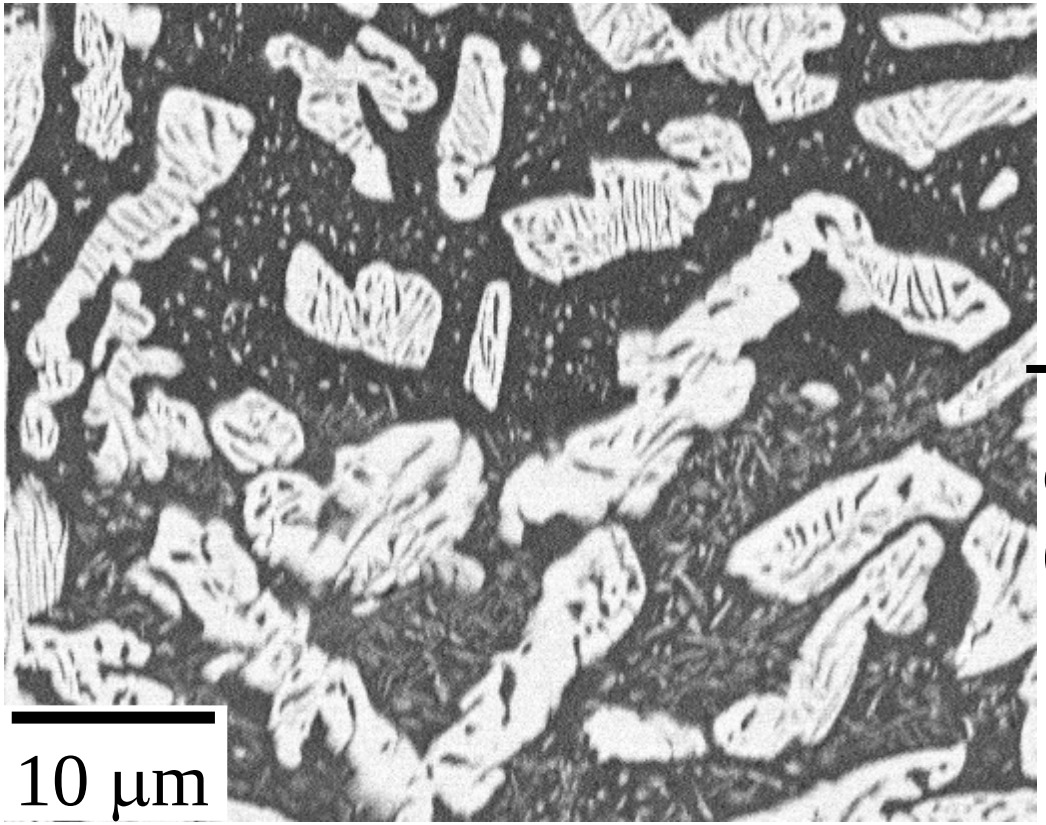


Cr_2N from nitrided Cr(Pt) matrix (dark)

Cr_3PtN from nitrided Cr_3Pt (white)

Coarse Cr_3Pt Dispersions Nitride Like Single-Phase Cr-Rich Cr_3Pt (Cr-17Pt) Alloy

SEM Cross-Section of (100) Oriented Cr-5Pt at.% Single Crystal Nitrided at 1000°C for 24h



Nitrided Cr(Pt) Matrix (dark gray)

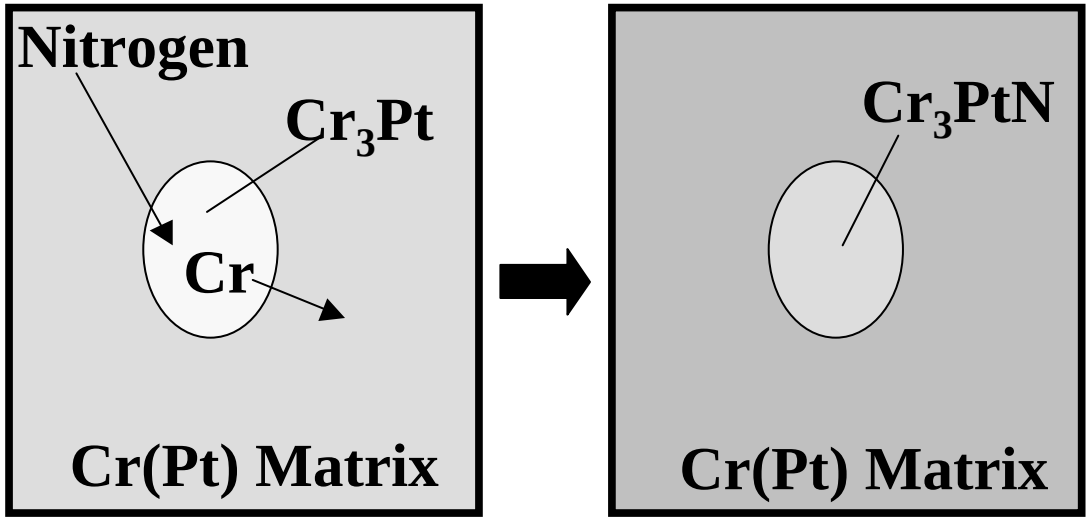
Nitrided Cr_3Pt (white)

Cr(Pt)-Metal Matrix (light gray)

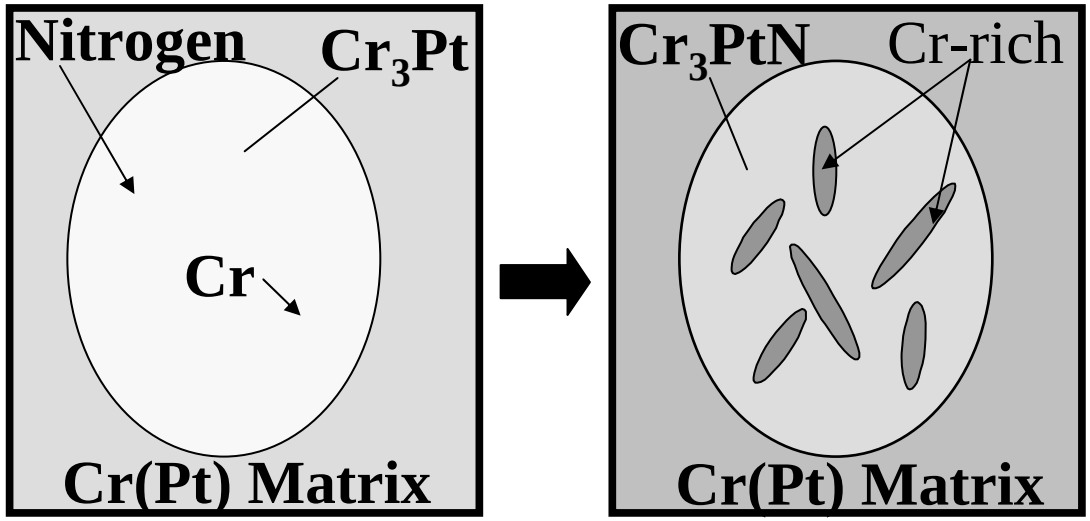
Nitrided Cr_3Pt (white)

Cr(Pt) Matrix Helps Accommodate Excess Cr During Nitridation When Cr_3Pt is Present as a <u>Fine</u> Dispersed Phase

- Proposed Mechanism for a Fine Cr_3Pt Particle



- Proposed Mechanism for a Coarse Cr_3Pt Particle



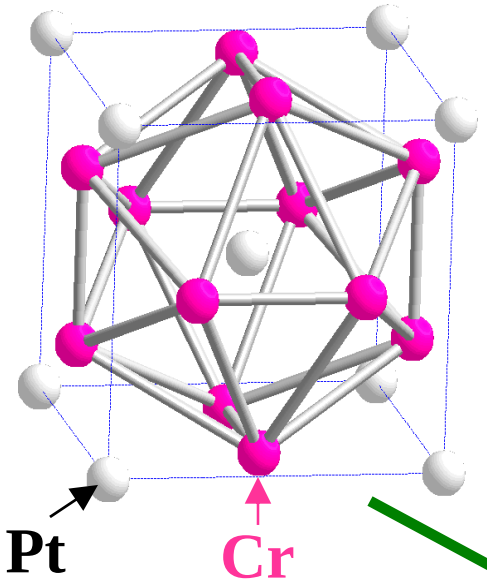
- Diffusion distance too great in coarse Cr_3Pt particle- behaves like single-phase Cr_3Pt alloy

How Did We Get to Cr_3PtN from Cr_3Pt?

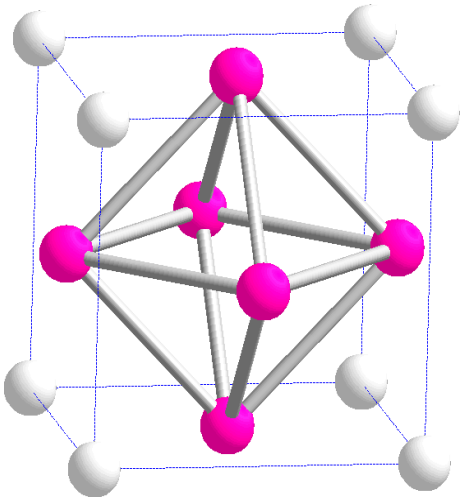
Look at Crystal Structures of Cr_3Pt and Cr_3PtN for Insights

Interstitial N into $L1_2$ Cr_3Pt Intermediary Yields Cr_3PtN Anti-Perovskite

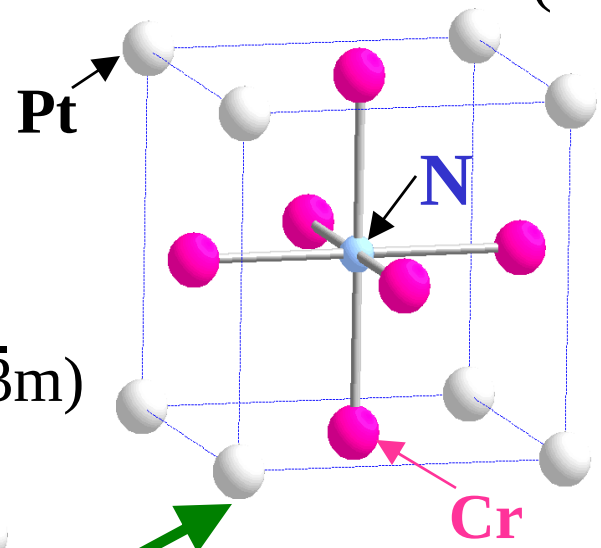
Cr_3Pt: BCC A15 ($Pm\bar{3}n$)



Cr_3Pt FCC $L1_2$ ($Pm\bar{3}m$)



Cr_3PtN Anti-Perovskite ($Pm\bar{3}m$)



- O,N,C impurities can stabilize $L1_2$ from A15: limiting case is perovskite
  - Stadelmeier, 1961; von Philipsborn and Laves, 1964
- XRD of as-received Cr-25Pt showed A15 with minor amounts of $L1_2$

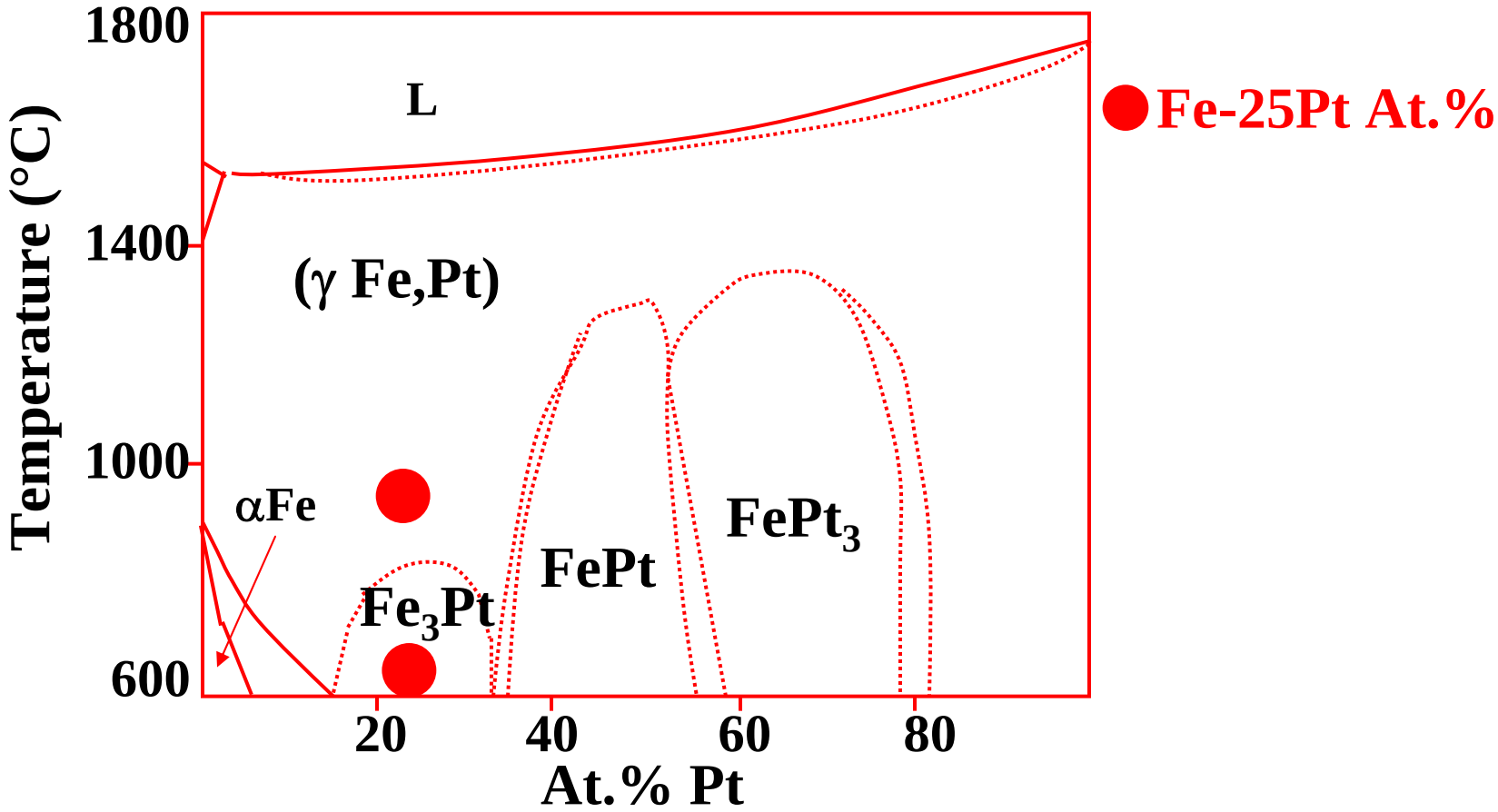
Suggests Reaction of $L1_2$ Precursors to Form Anti-Perovskite Structures

- Trying to establish guidelines to identify systems amenable to this approach

- Is the precursor intermetallic structure really important or is the metal component stoichiometry the key?

- Are these phenomena widespread or is Cr-Cr_3Pt an isolated case?

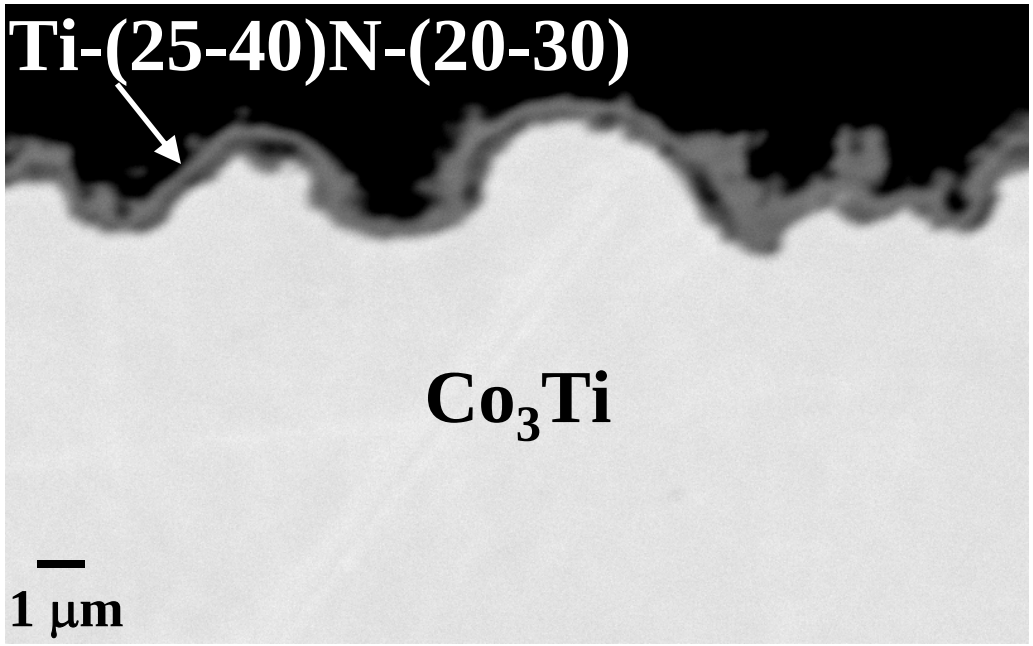
Fe_3PtN Formed With and Without $L1_2$ Fe_3Pt Precursor



- Fe_3PtN anti-perovskite by nitriding Fe-25Pt at 575°C **and** 950°C in NH_3
- 575°C: $L1_2$ Fe_3Pt means Fe_3PtN is interstitial analog
- 950°C: γ (Fe,Pt) is FCC $Fm\bar{3}m$; Fe_3PtN **related** but not exact analog

$L1_2$ Co_3Ti Did Not Form a Complex Nitride

SEM Cross-Section of $L1_2$ Co_3Ti Nitrided at 900°C, 24 h, N_2-$4H_2$



- No previously reported anti-perovskite Co_3TiN phase
  - trying to form a new phase
- Selective oxidation occurred to form Ti-N-O
  - Why didn't an anti-perovskite form?

Speculation on Some Possibilities

- Did oxygen impurities trigger the selective oxidation of Ti and prevent complex nitride phase formation?
  - -oxygen too electronegative, don't see as many interstitial type phases as with N and C
  - -Ti-oxides very stable, difficult to reduce oxygen impurities to achieve a purely nitriding environment

- Is TiN too stable? Was the driving force for TiN formation too great relative to the desired interstitial nitrogen penetration into Co_3Ti?
  - -Note: Cr-nitrides are not very stable, much less competition

- Structure: In Cr_3PtN, the nitride-forming element Cr is the nearest neighbor with the interstitial N. In a speculated Co_3TiN phase, the non-nitride forming element, Co, would be the nearest neighbor for the N, which would be less energetically favored (Payzant)

Also Exploring non $L1_2$ Precursor Systems

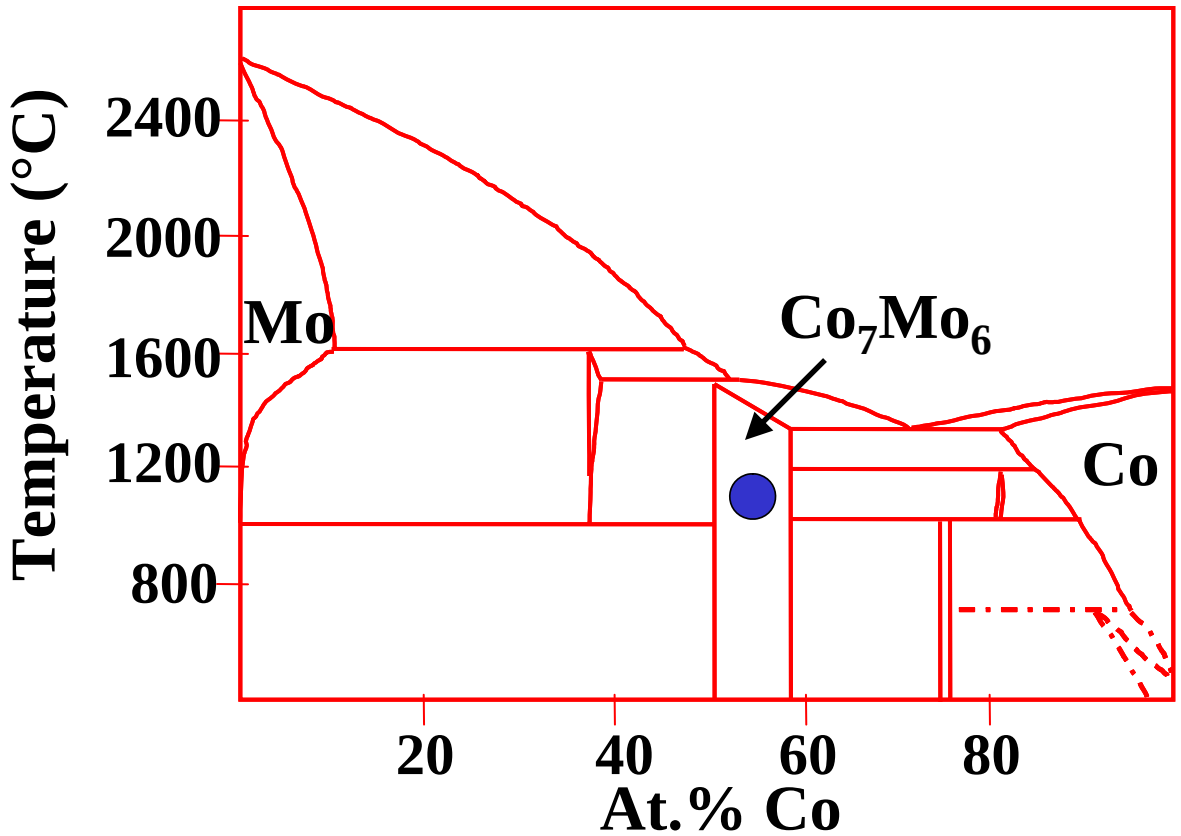
Specifically Looking to Form New Phases in Some Technologically Interesting Systems

Mo-Co/Mo-Ni Carbides and Nitrides of Increasing Interest as Catalysts

Co_6Mo_6C, $Co_6Mo_6C_2$, Ni_2Mo_3N, etc

- **Hydrotreating Removal of S, N, and O Impurities from Fossil Fuel Feedstocks**
- **Ammonia Synthesis**
- **Water Gas Shift ($CO + H_2O \rightarrow CO_2 + H_2$) Fuel Processing to Make H_2**

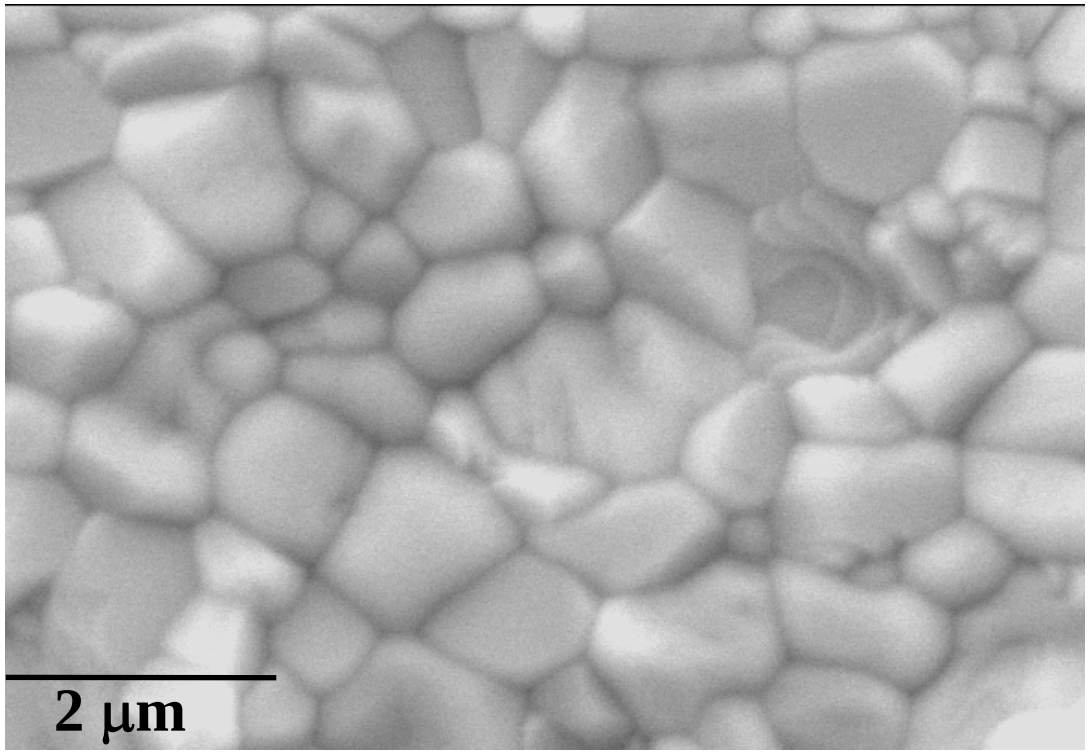
Can We Make $Co_6Mo_6C_2$ by Carburizing Co_7Mo_6?



- Co_7Mo_6 Intermetallic has ~1:1 Stoichiometry of $Co_6Mo_6C_2$
- Intermetallic/carbide not exact interstitial analogs
  - -Co_7Mo_6 is rhombohedral ($R\bar{3}MH$)
  - -$Co_6Mo_6C_2$ is a diamond cubic ($FD\bar{3}MS$; 122 atoms/unit cell)

$Co_6Mo_6C_2$ Formed by Carburizing Co_7Mo_6 Intermetallic Alloy

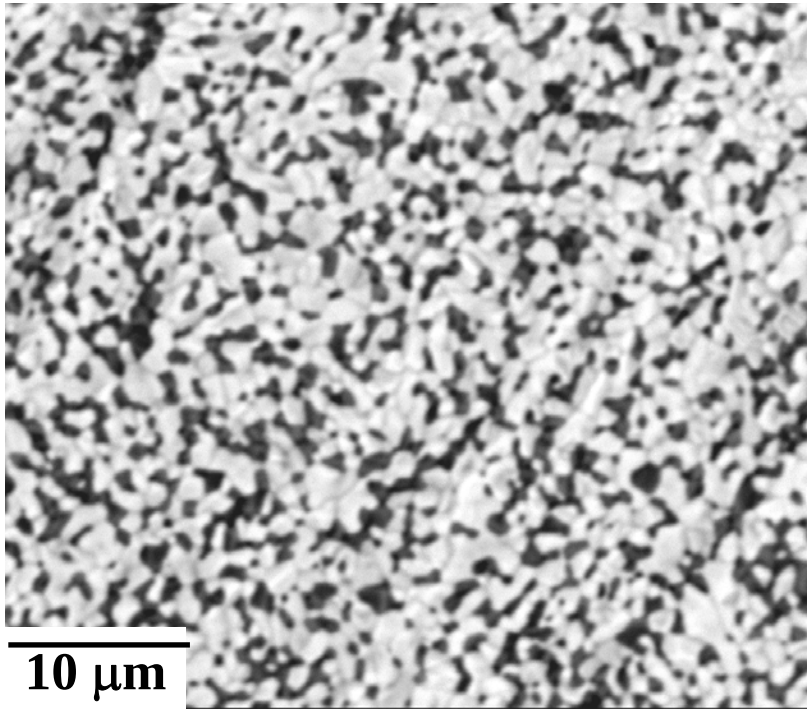
SEM Surface of Co-45Mo after Carburization at 1050°C



- Composition of 45Co-42Mo-13C at.%
  - -XRD consistent with slightly carbon-lean $Co_6Mo_6C_2$
- Planning to carburize powders to measure catalytic activity and compare with material made from oxide precursors

$Co_6Mo_6C_2$ + Co Composite Surface by Carburizing CoMo + Co Alloy

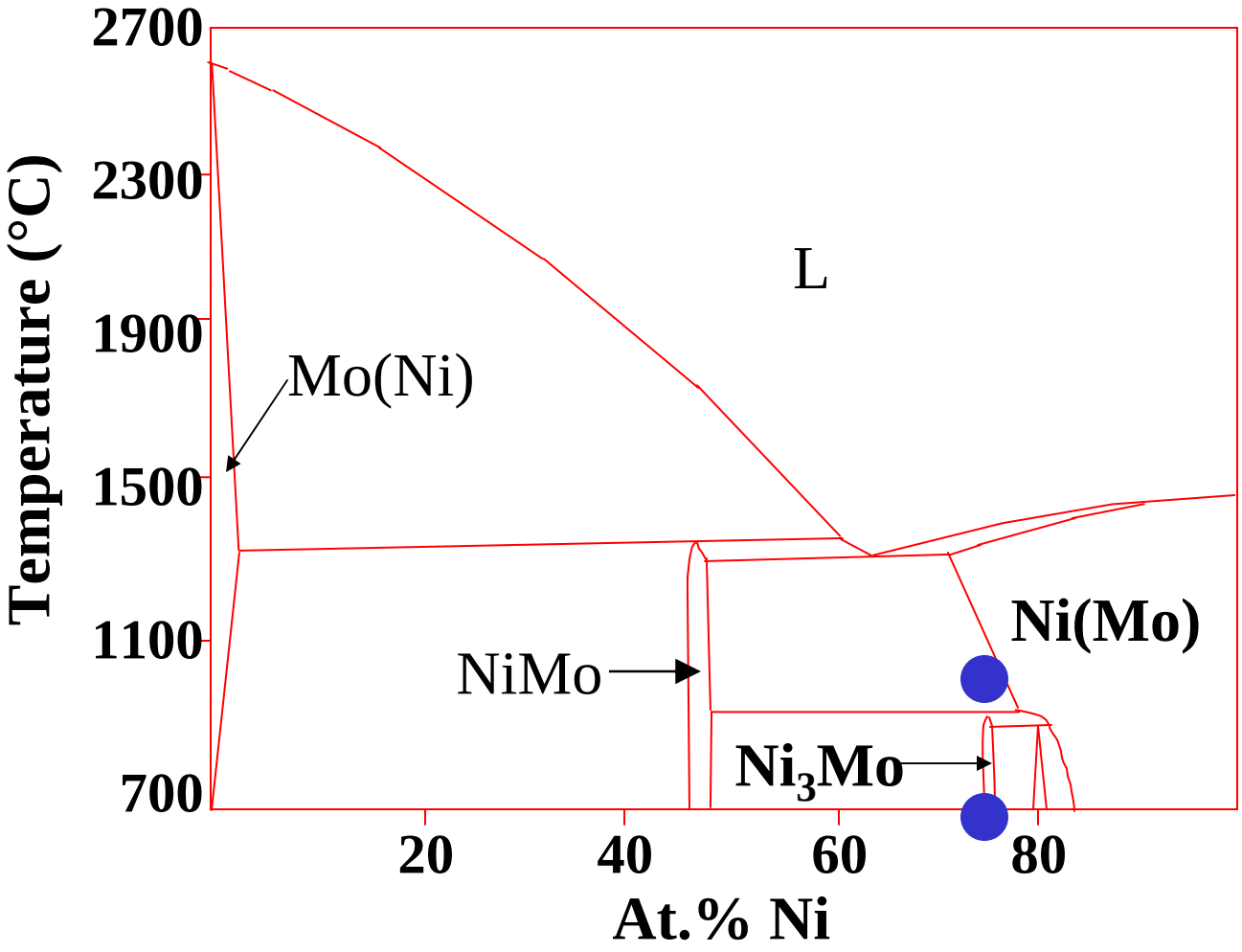
SEM Surface of Co-25Mo After Carburization at 1050°C



$Co_6Mo_6C_2$ (light)
Co (dark)

- May have aspects of in-place reaction

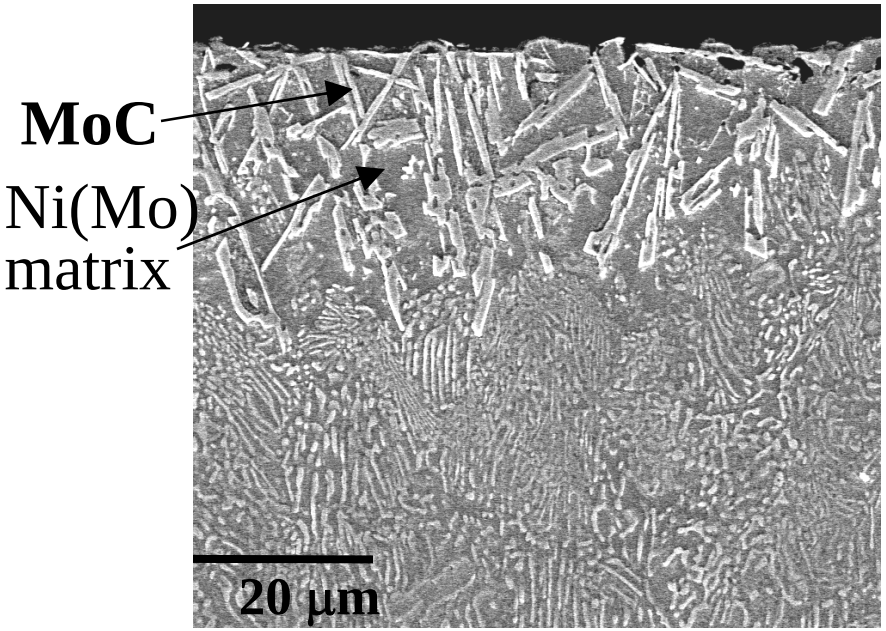
Attempt Formation of "New" Complex Nitride Phase in the Mo-Ni System



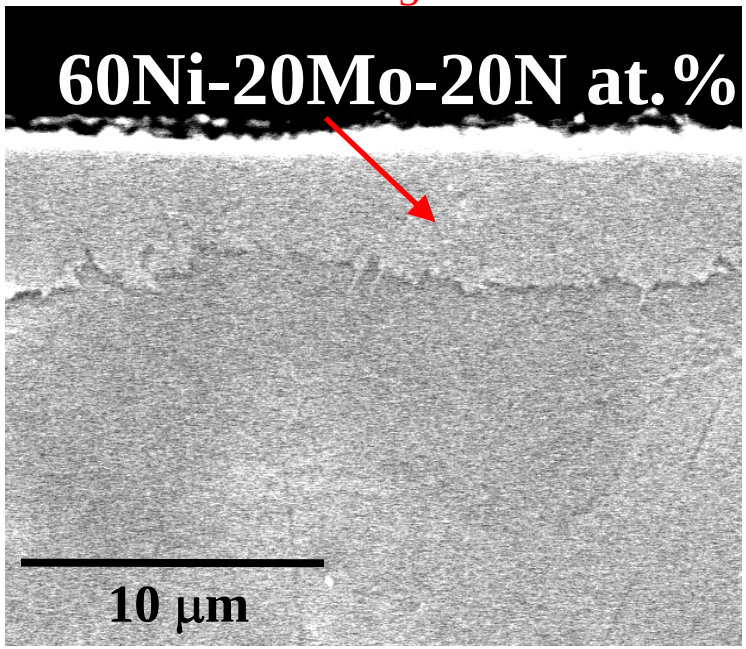
- No record found for a nitride with the 3Ni:1Mo ratio
- Nitride Ni-25Mo at 575°C (Ni_3Mo stable) and 950°C [Ni(Mo) stable]

“New” Nitride of Stoichiometry Ni_3MoN Formed on Nitriding Ni_3Mo at 575°C

950°C: Ni(Mo)



575°C: Ni_3Mo



- “Ni_3MoN” very preliminary and based solely on SEM/EPMA
- Nitriding at 950°C where Ni(Mo) was stable yielded Ni + MoC

Insights Thus Far for Selecting Precursor Intermetallic Compounds

- Stoichiometry of the precursor intermetallic is very important

- An exact interstitial analog between precursor intermetallic and resultant complex phase is not needed, however, the more similar the better

- Complex phase formation appears more likely with precursor intermetallic component elements of relatively low stability with the oxidant

Concluding Remarks: Oxidation As a Synthesis Approach

- Well Established in Semiconductor and Wear Industries
  - -selective oxidation to form insulating oxide surfaces (e.g. work of Mike Graham in our community)
  - -internal/external oxidation processes for surface hardening

- Long Utilized by Solid-State Chemists and Ceramists
  - -thick film/bulk ceramics by complete oxidation of alloy precursors (e.g. work of Yurek, Sandhage, etc.)

- Leveraging metallurgical aspects of the precursor alloy (crystal structure, phase equlibria, precipitation, etc.) may expand upon the number and types of phases that can be formed and provide a way to control how they arrange themselves

Many People Contributed to This Work

Ian Anderson (phase analysis, concepts)
David Hoelzer (TEM, phase transformations)
Tom Lograsso (Cr-Cr_3Pt single-crystals)
Karren More (TEM, scale structures)
Andrew Payzant (crystallography, concepts)
Bruce Pint (scale microstructure interpretation)
Bob Rapp (oxidation issues)
Pete Tortorelli (concepts)
Larry Walker (EPMA)
Ian Wright (concepts)
Sarah Wrobel (Cr-Cr_3Pt nitridation)
Bing Yang (nitrided bipolar plates)
David Young (concepts, experiment interpretation)

- DOE Fossil Energy Advanced Research Materials Program
- ORNL SEED Program
- DOE Hydrogen, Fuel Cell, and Infrastructure Program

Thank You for Your Attention!