Templated Growth of Complex Nitride Island Dispersions by Controlled Internal Reactions

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Goal: New Synthesis Approach to Complex Ceramic Dispersions

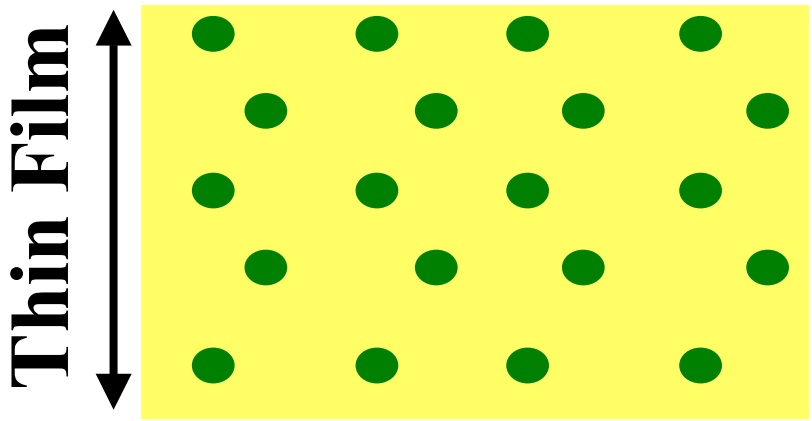
- Background: Proposed Synthesis Concept
  - -Based on internal reactions in two-phase metallic alloys

- Model System: Cr_3Pt in Cr as precursor to Cr_3PtN perovskite in Cr/Cr_2N by internal nitridation
  - -Details of reaction mechanism

- Potential Applicability to Other Systems
  - -Preliminary results for nitrided $Fe_{17}Nd_2$ in Fe

- Will This Work for Nanoscale Synthesis?

Motivation: Nanodispersed Complex Ceramic Phases of Scientific and Technological Interest

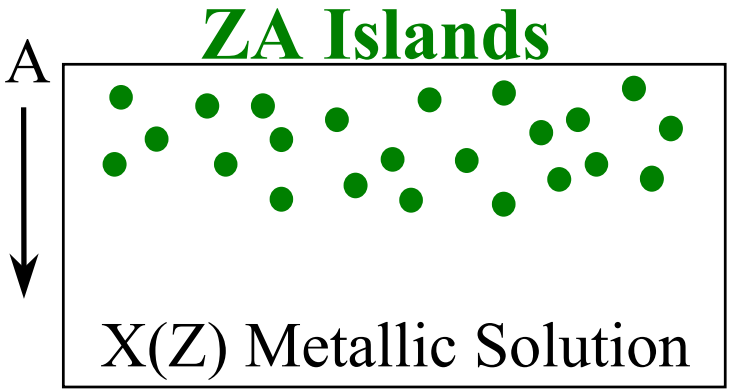


Complex (at least ternary) Ceramic (1-100 nm)

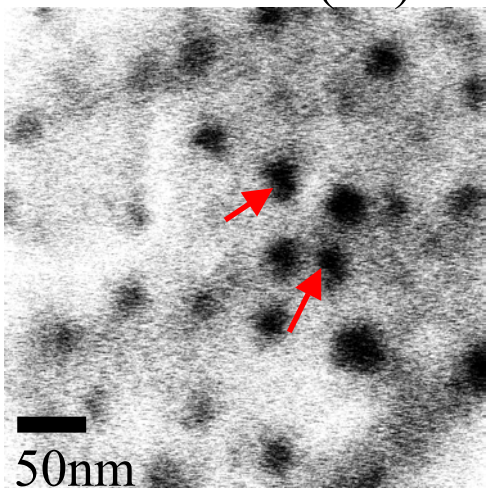
Metal or Simple Ceramic Matrix

- Interesting and potentially useful electrical, optical, magnetic, etc. behaviors emerge at the nanoscale
- **Very difficult to make: many complex ceramic phases not currently accessible in dispersed architectures**

Internal Reactions in Metallic Alloys Great Way to Make Ceramic Nanodispersions



Fe-oxide in Pd by Internal Oxidation of Pd(Fe) Alloy

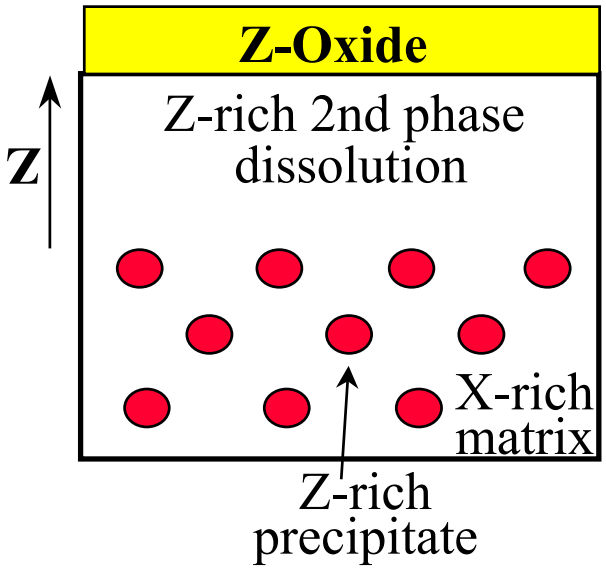


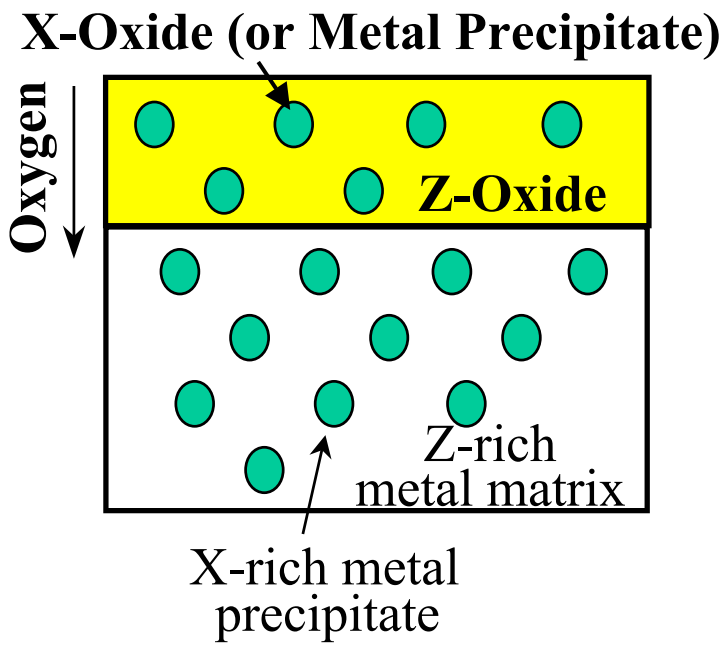
(SEM X-section)

- Simple and rapid method: applicable to large scale surface coverage (oxidation, nitridation, sulfidation, etc.)
- Generally Amenable only to Simple (Binary) Ceramic dispersions: Limited interest for functional behaviors

Reaction in Two-Phase Alloys May Provide Route to Form Complex Ceramic Phases

Limiting Cases





Cooperative Mode **Independent**

- Cooperative: Single-Phase Reaction Product, Desirable for Metal Protection in Aggressive High-Temperature Environments
- Independent (**In-Place**): Composite Surface Which Mimics Underlying Alloy Structure, "Bad" for Metal Protection, **BUT...**

We Can Use Initial Two-Phase Metal Structure as a Template for Complex Ceramic Island Synthesis

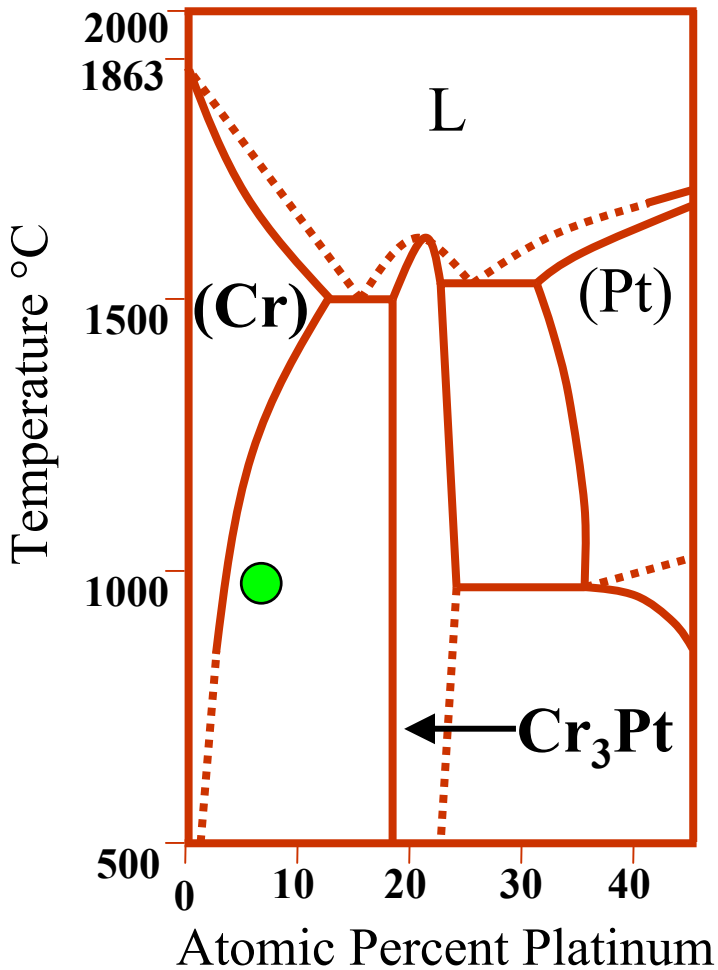
- In-place internal reaction **replicates** the **size**, shape, location, and **chemistry** of each phase in the initial metallic structure

- If the second phase dispersion is a **metallic compound** then a **complex** ceramic phase dispersion with a **similar metal component stoichiometry** can potentially be formed

- High degree of control possible via initial two-phase metallic template: **leverage versatility of metallic phase equilibria** (solid state precipitation, crystallographic relationships, etc.)

Potential to Synthesize New Structures Not Achievable by Other Means

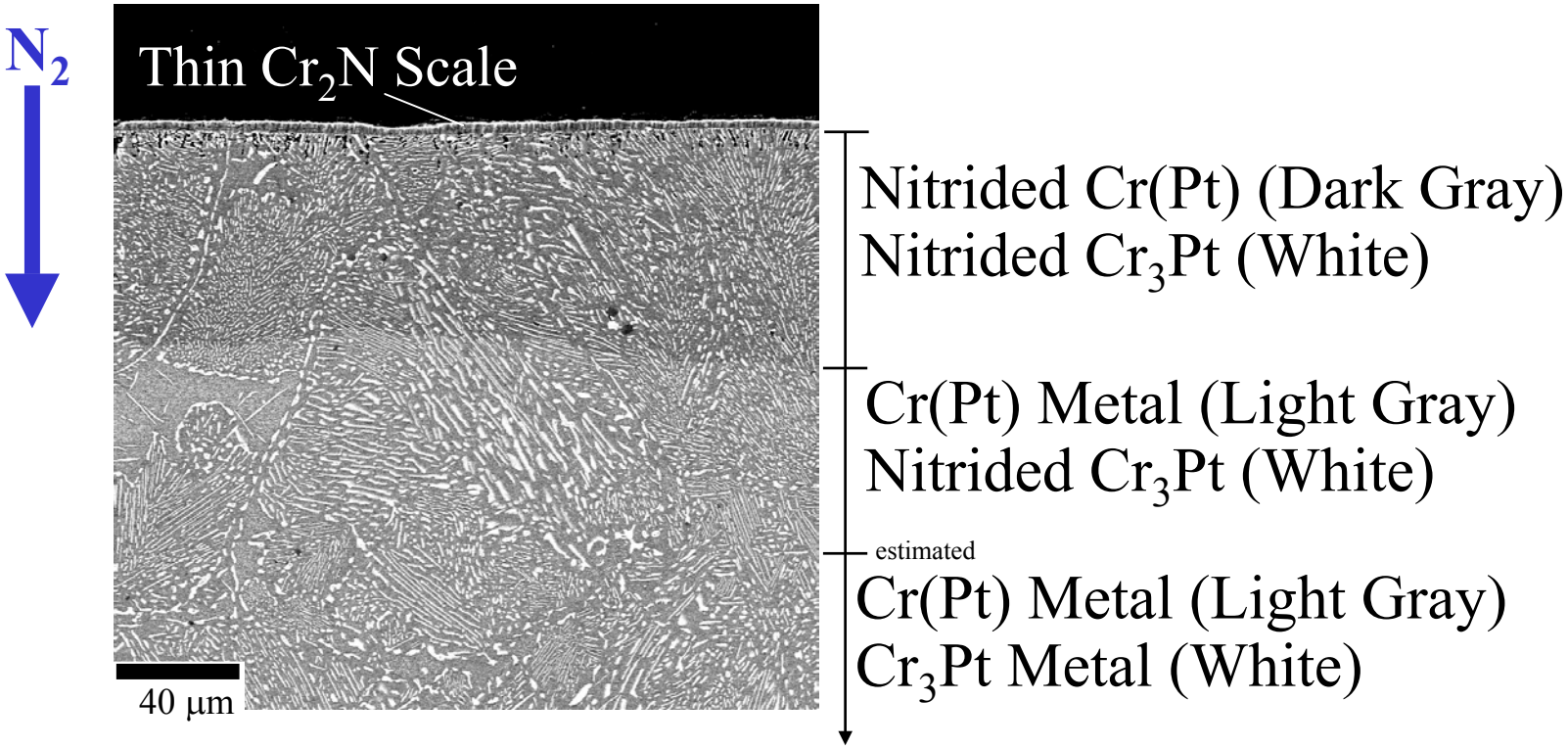
Proof of Principle: Can We Form Cr_3PtN Perovskite by Nitridation of Cr_3Pt-Dispersed Cr?



- 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
- 95Cr-5Pt at.% selected for study

95Cr-5Pt at.% Exhibited In-Place Internal Nitridation After 24h at 1000ºC in Nitrogen

SEM cross-section micrograph

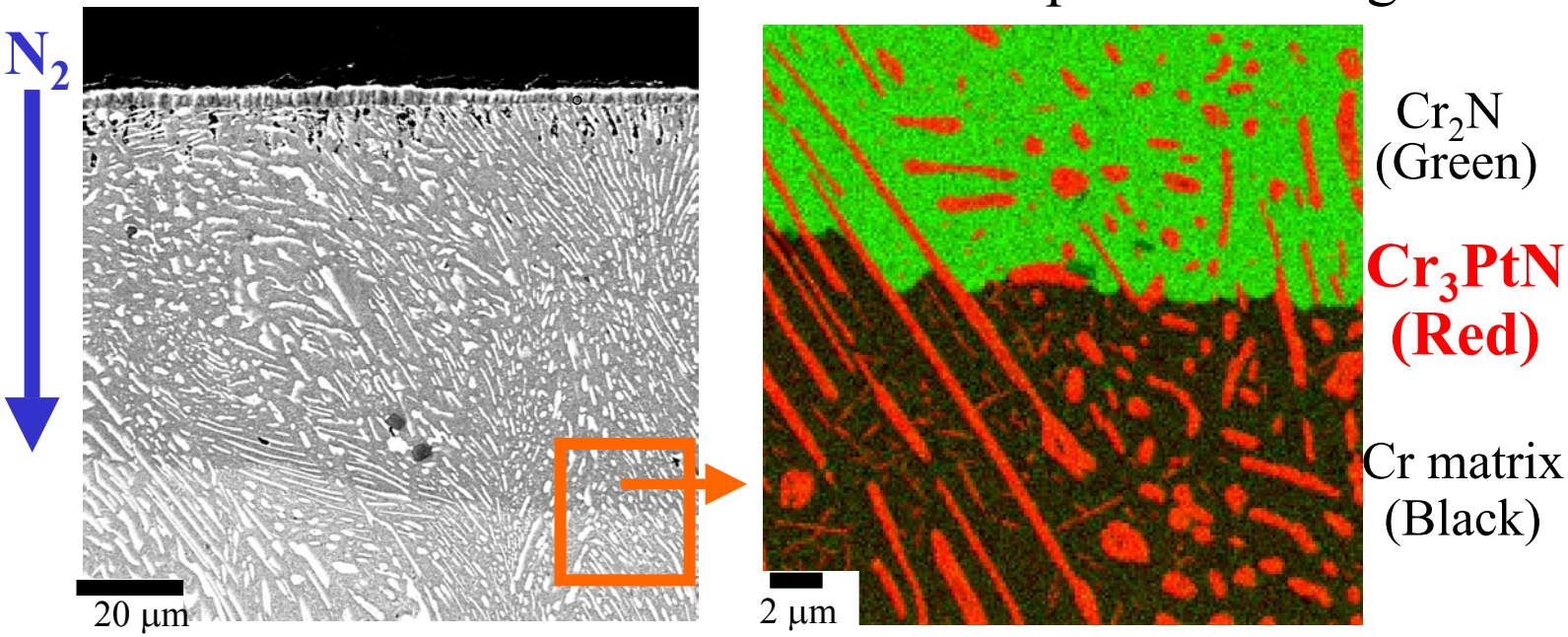


- Reaction exactly followed underlying alloy microstructure
- Cr_3Pt phase nitrided to a greater depth than Cr matrix phase

Microprobe, XRD, TEM Data Consistent with In-Place Internal Nitridation of Cr_3Pt Dispersion to Form Cr_3PtN

SEM Cross-Section

LV-EDX Spectrum Image



- No evidence of Cr_3Pt internally nitriding to form Cr_2N+Pt
- Proof of principle to form complex phase established

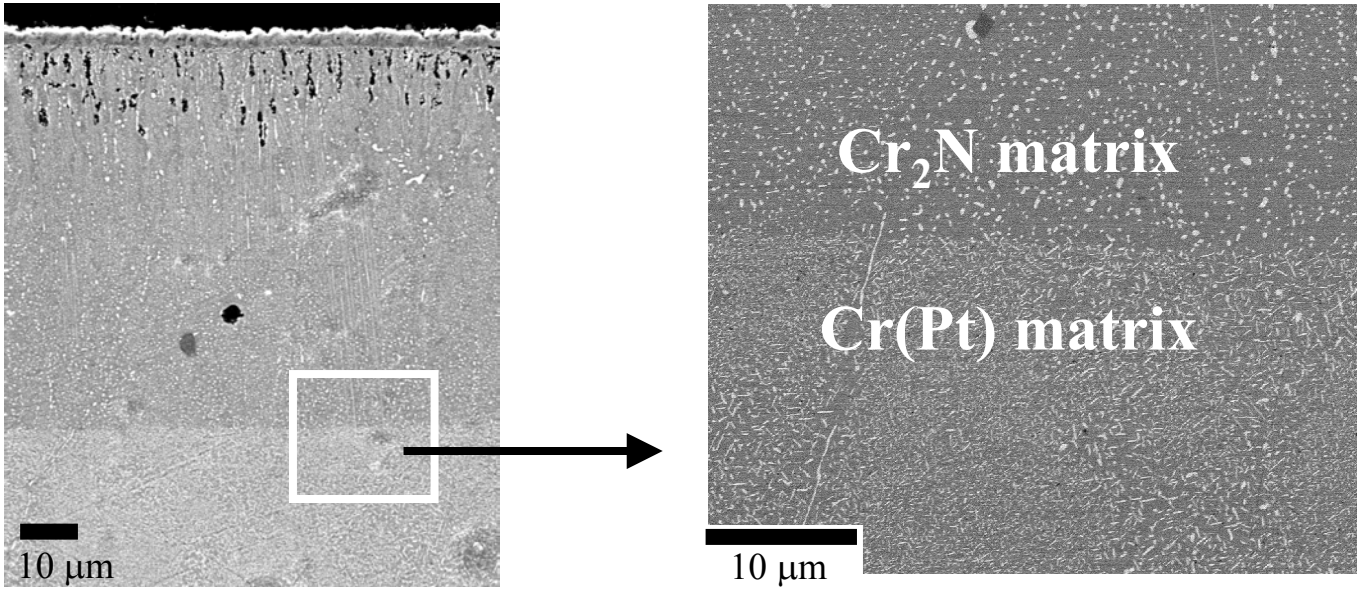
What About Mechanistic Details?

Gain insight through nitridation of single-phase Cr(Pt) and Cr_3Pt alloys

- Cr(Pt): 98Cr-2 Pt at. %
- Cr_3Pt: 83Cr-17 Pt at. %
- Alloys selected to extend slightly into two-phase field (sets component activities)

"Single Phase" Cr(Pt) Alloy Exhibited Similar Nitrided Structure to Two-Phase Cr(Pt)+Cr_3Pt

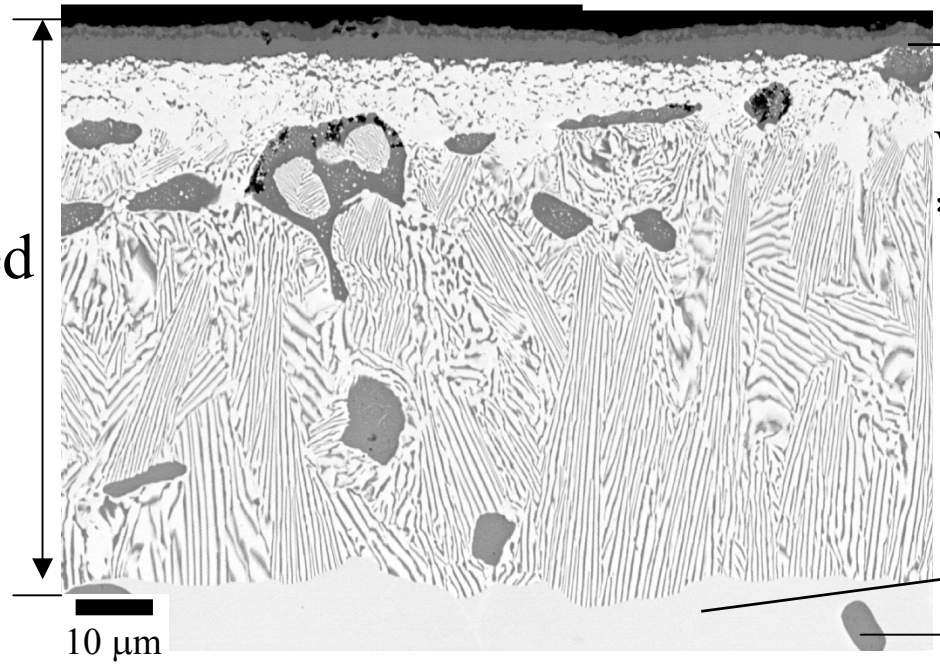
Cross-section SEM micrographs of 98Cr-2Pt at.% after 24h at 1000°C in nitrogen



- Reaction dominated by high nitrogen permeability in Cr(Pt)
- Analysis of fine second phase dispersion in progress, XRD consistent with Cr_3PtN

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

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



Cr_2N

White phase: Cr_3PtN
*63Cr-19Pt-18N at.%

Dark lamellar Phase:
*84Cr-13Pt-3N at.%

Cr_3Pt Matrix (light)

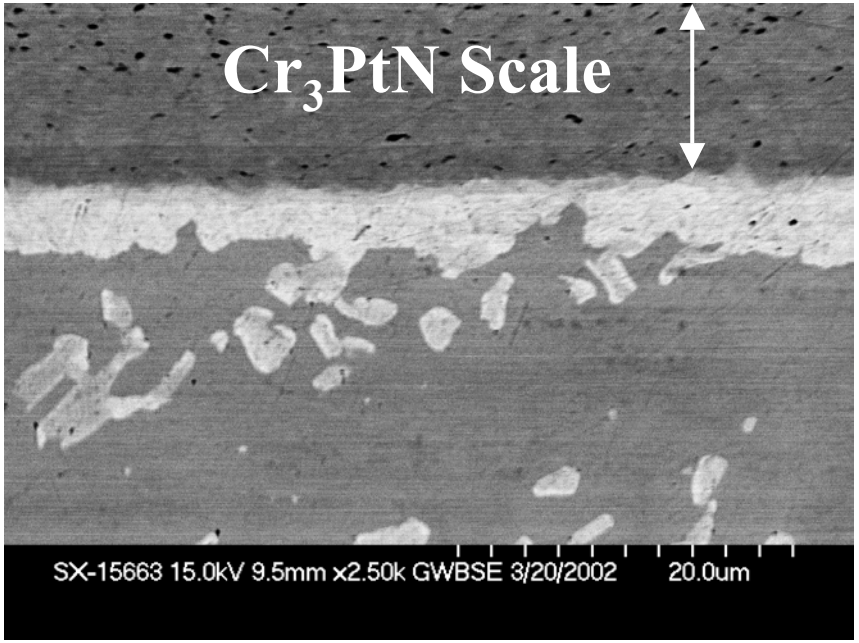
Cr(Pt) Phase

*Microprobe data semiquantitative due to fine scale

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

Nitridation of Cr-Lean Cr_3Pt Consistent with Proposed Mechanism

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



Pt_3Cr (light)

Cr_3Pt matrix (dark)

- Cr-lean Cr_3Pt in two-phase Cr_3Pt + Pt_3Cr field
- 75Cr-25Pt alloy yields nearly direct Cr_3PtN scale formation (some Pt rejection)

Why Do We See "Single-Phase" Cr_3PtN from Cr-rich Cr_3Pt Phase in 95Cr-5Pt?

- Cr(Pt) matrix helps accommodates excess Cr during nitridation when Cr_3Pt is present as a dispersed phase (limited to fine Cr_3Pt particles/small diffusion distance)

- Close to, but not ideal, in-place internal nitridation in the Cr(Pt)-Cr_3Pt System

- Template Effect Worked- Cr_3Pt precipitates converted to Cr_3PtN dispersions

Prerequisites as Synthesis Approach

- Availability of solid state precipitation reaction (or other means) to form initial two-phase metallic template

- Metallic matrix phase with a high oxidant permeability (favors internal reaction modes)

- Existence of precursor metallic compound phase with desired complex ceramic phase stoichiometry

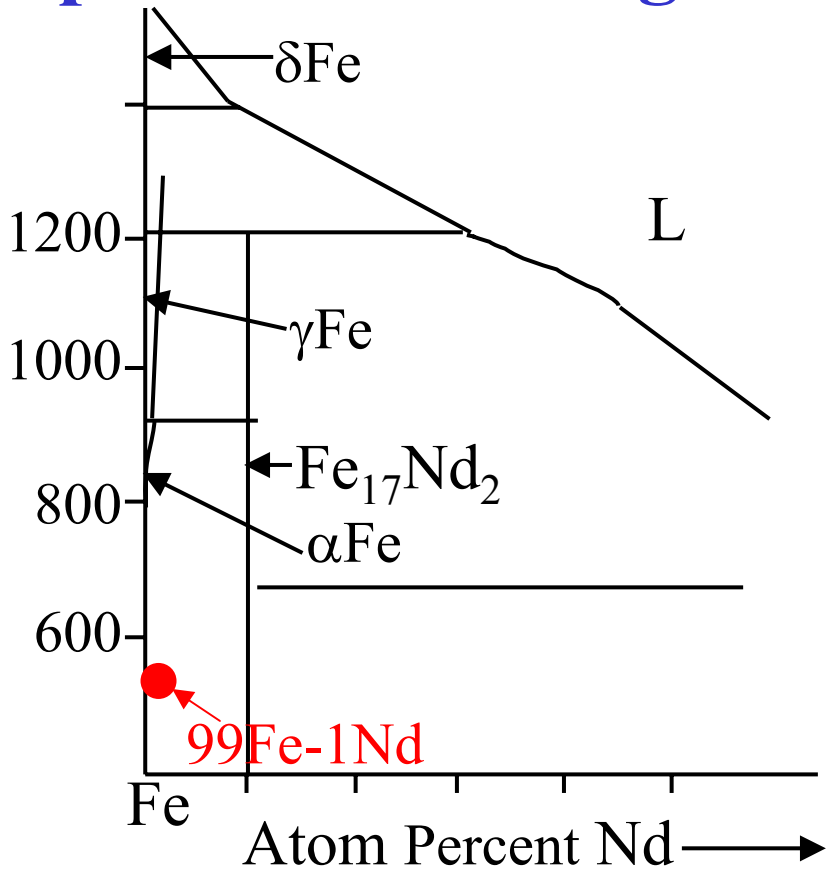
Not all systems will exhibit in-place internal reaction

Some Potential Candidate Precursor Systems

Base Metal	Potential Precursor Phase
Al	Al_2Cu, AlLi, Al_3Sc
Co	Co_7Hf_2, Co_3Nb, Co_3Ti, Co_3W, CoZn
Cr	Cr_3Ge, Cr_3Pt, Cr_3Rh, Cr_2Ti
Cu	Cu_2In, Cu_4Ti
Fe	$Fe_{17}Er_2$, Fe_2Mo, $Fe_{17}Nd_2$, Fe_2Nb, $Fe_{1-x}Se$, Fe_2Ta, Fe_2Ti, Fe_2W
Gd	Gd_2In
Ge	Ge_2Hf, Ge_5La_3
Hf	Hf_2Al, Hf_3Ge, Hf_3Mn_2, Hf_2Pd, HfRe, HfV_2, HfW_2
Ir	Ir_3Hf, Ir_3Zr
La	La_3In
Mn	Mn_2Hf, Mn_2Sb, Mn_2Ti
Mo	Mo_2Co, $MoPd_2$, MoPt, MoRh, MoRu, Mo_3Si, Mo_2Zr
Ni	$Ni_{17}Gd_2$, Ni_3In, Ni_3Nb, Ni_3Sn, Ni_8Ta
Nb	NbFe, Nb_6Ge, Nb_3Sb, Nb_5Si_3, $NbSn_2$
Pd	Pd_3Ta
Pr	PrZn
Re	$Re_{24}Ti_5$, $Re_{24}Zr_5$
Ru	RuTi
Ta	TaFe, Ta_2Ni, TaPd
Ti	Ti_3Bi, Ti_2Co, $TiCr_2$, Ti_2Cu, TiFe, Ti_5Ge_3, Ti_3Ir, TiMn, Ti_2Ni,Ti_4Pb, Ti_4Pd, Ti_3Pt, Ti_4Sb
V	V_3Ge, V_2Hf, V_3Ni, V_2Zr
W	W_2Zr
Zr	Zr_3Al, Zr_2Bi, Zr_2Co, $ZrCr_2$, Zr_4Fe, Zr_3In, $ZrMn_2$, Zr_2Pd, Zr_2Pt, Zr_2Re, ZrRu, ZrV_2, ZrW_2, Zr_2Zn

- Intermetallic nitrides, carbides, borides appear very accessible
- Ternary and higher order precursors also amenable: greatly increases number of potential systems

Internal Nitridation of $Fe_{17}Nd_2$ Dispersed Fe to Model Synthesis of Intermetallic Nitride Dispersions for Magnetic Properties

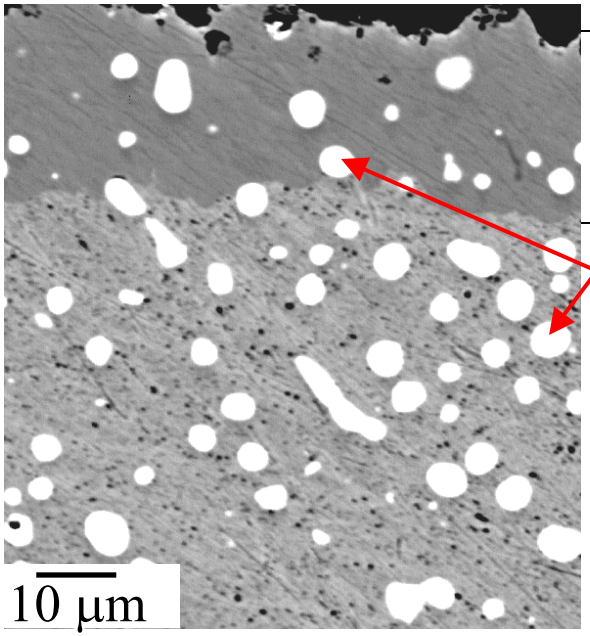


•Goal is hard magnetic intermetallic nitride phase nanodispersions in hard/soft/non magnetic simple ceramic or metallic matrices

In-Place Internal Nitridation of $Fe_{17}Nd_2$-Dispersed Fe Possible

Backscatter SEM Cross-Section of Nitrided 99Fe-1Nd at.%

Nitrogen



Fe_4N (dark)

$Fe_{17}Nd_2N_5$
(white dispersion)

Fe Metal (light gray)

•Coarse structure derived from arc-cast/annealed material

*Preliminary Phase I.D. Based Solely on Compositions Data

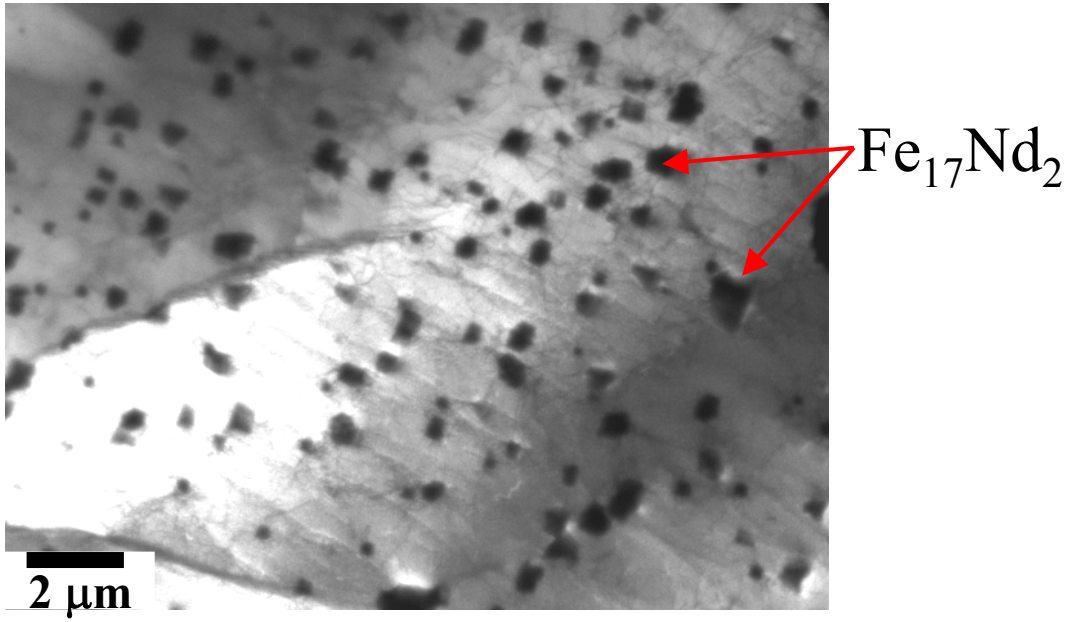
What About Nano???

Can we create **Nano/Meso** scale metallic precipitates for precursor template?

- Thin Films (metastable/amorphous precursor parent solutions)
- Rapid Solidification/Quenching
- Some Precedence for Nano Metal Precipitates:
  - -Fe-B based magnetic alloys (e.g. NANOPERM)
  - -Al_3Sc precipitation-strengthened Al

First Attempt at Rapid Solidification Yielded 500 nm Range $Fe_{17}Nd_2$ Precipitates

TEM View of Melt Spun and Annealed 99Fe-1Nd at.%



- Order of magnitude finer structure than cast material
- Need additional order of magnitude refinement to elicit "nano" effects

Conclusions

- In-Place Internal Reaction approach shows potential for micro scale synthesis of complex ceramic dispersions
  - -Complex intermetallic nitrides, carbides, borides

- Jury still out as nanosynthesis approach