

Investigation of Internal Oxidation in Two-Phase Alloys as a Synthesis Approach to Templated Growth of Complex Ceramic Island Structures

M.P. Brady, *S.K. Baham, D.T. Hoelzer, E.A. Payzant,
P.F. Tortorelli, I.M. Anderson, and J.A. Horton

Metals and Ceramics Division
Oak Ridge National Lab

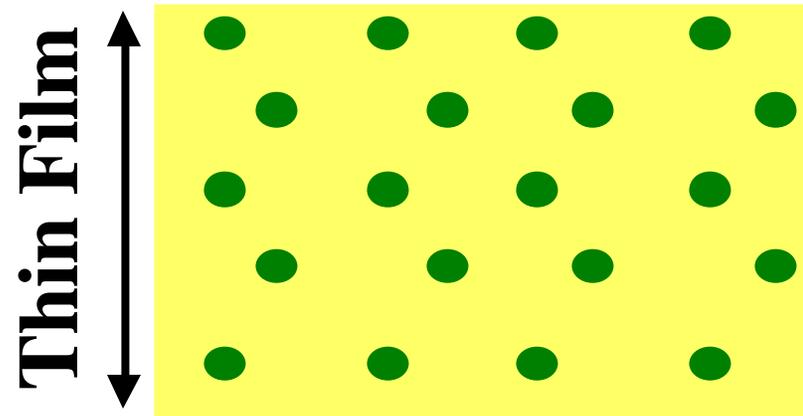
*Department of Materials Science and Engineering
University of Tennessee, Knoxville

bradymp@ornl.gov, sbaham@utk.edu

Abstract

A new synthesis route, based on the in-place form of internal oxidation in multi-phase alloys, is proposed for the formation of complex ceramic island dispersions, potentially on the nano scale. The key characteristic of in-place internal oxidation is that the reaction product replicates the size, morphology, spatial distribution, and chemistry of each phase in the underlying alloy structure. Effectively, the initial alloy microstructure acts as a template. If the second phase is a compound, we propose that a complex ceramic phase with a similar metal component stoichiometry can potentially be formed. Using this approach, a micro-dispersion of a complex nitride perovskite, Cr_3PtN , was formed in Cr_2N or Cr(Pt) by internal nitridation of a two-phase $\text{Cr(Pt)} + \text{Cr}_3\text{Pt}$ precursor alloy.

Nanocomposite Surfaces of Complex Ceramic Phase Islands of Great Interest For Functional Applications



Complex (at least ternary) Ceramic (1-100 nm) ●
Metal or Ceramic Matrix ■

- **Interesting magnetic, optical, electrical properties**
- **Very difficult to make-new approaches needed**

Internal Oxidation Reactions are a Great Way to Make Ceramic Island Dispersions

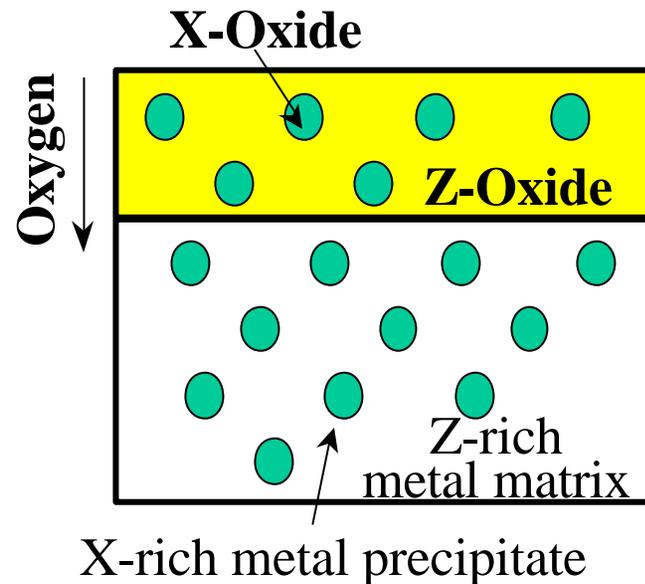
- **Rapid, cheap, and controllable (especially if only need to oxidize thin metallic film)**
- **Also applicable to nitridation, carburization, etc.**

But

- **Generally limited to direct, controllable formation of only simple (binary) ceramic phases**
- **Complex ceramic phase disperisons (e.g. ternary perovskites) more interesting for functional applications**

Internal Oxidation in Two-Phase Alloys May Offer Solution to Synthesis of Complex Phases

*In-Place Mode of Internal Oxidation



- **Form of internal oxidation unique to multi-phase alloys**
- **Oxidant inward diffusion \gg alloy component diffusion**
- **Phases oxidize **independently**: Yields composite in which scale **replicates** initial alloy microstructure**

*After Gesmundo and co-workers

Use Initial Two-Phase Alloy Microstructure as a Template

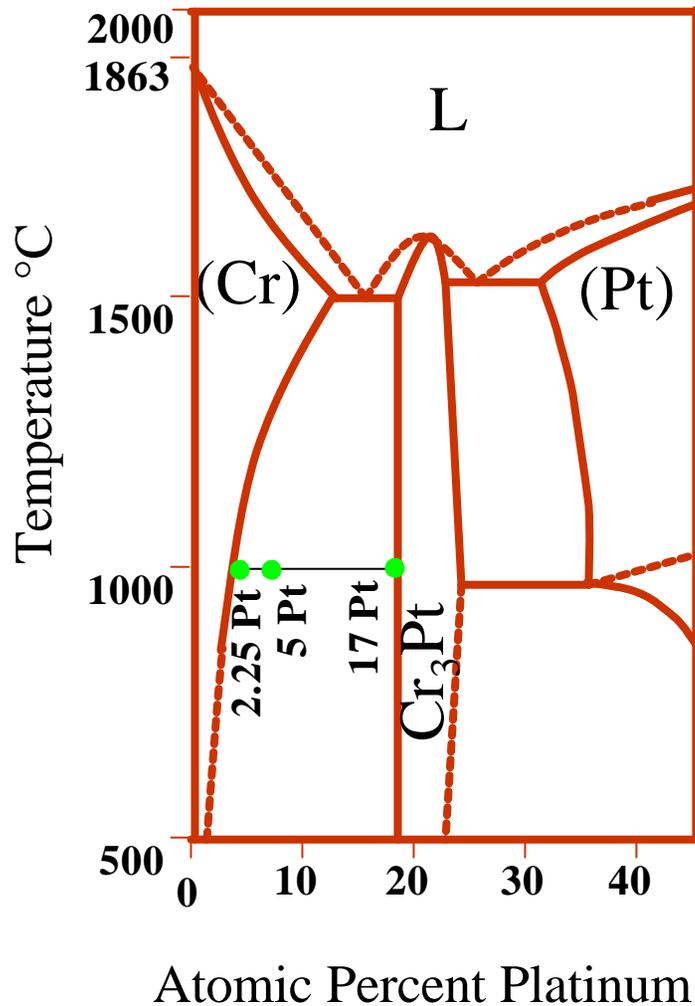
In-place mode of internal oxidation replicates the size, shape, location, and chemistry of each phase in the initial alloy microstructure

- In-place internal oxidation with a second phase compound precipitate can potentially yield a complex ceramic phase of similar metal component stoichiometry
- If the precursor compound phase can be precipitated on the nanoscale, then the complex ceramic dispersion can potentially be formed on the nanoscale (likely possible only for thin films)

Goal

- Determine if the in-place mode of internal oxidation in a two-phase alloy can be used to controllably yield a complex ceramic dispersion.
- Understand the mechanism by studying the oxidation behavior of the phases individually and in combination.

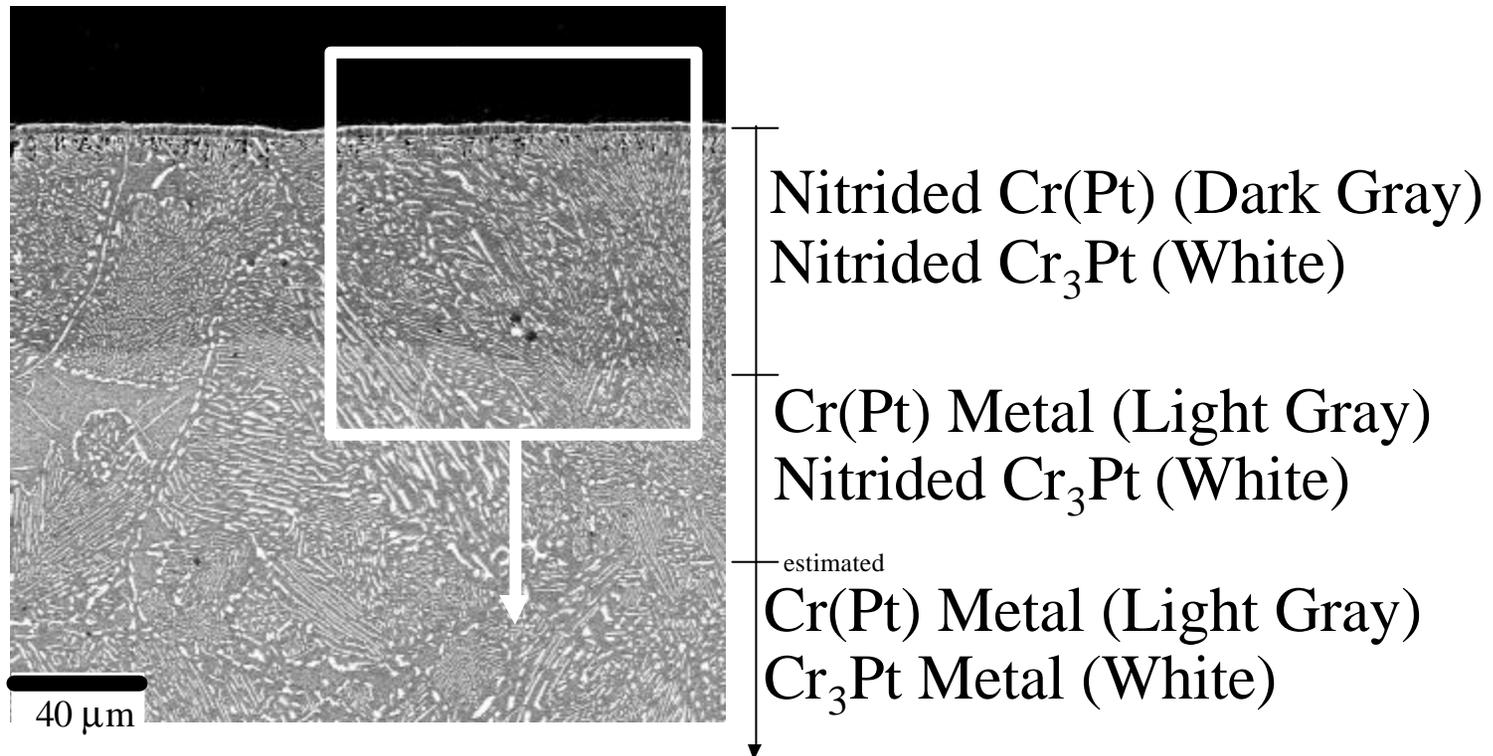
Nitridation of Model Two-Phase Cr-Pt Alloys Selected for Proof of Principle Study



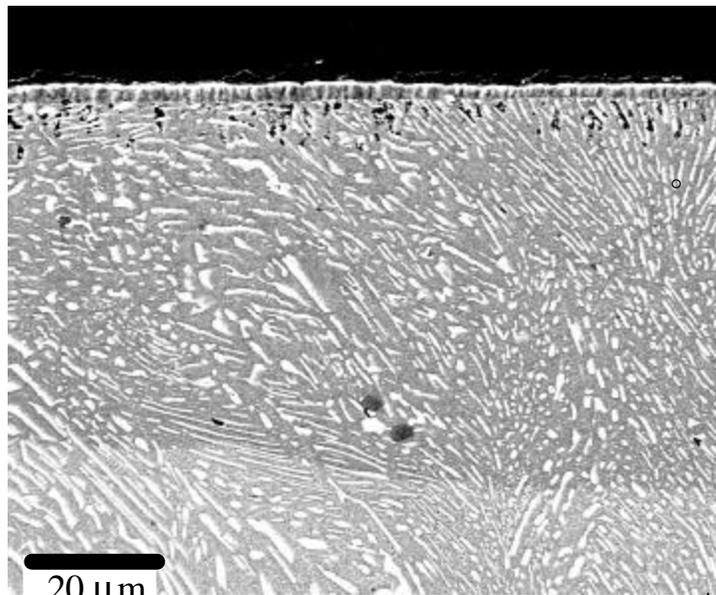
- Cr exhibits high permeability to nitrogen
- Two-phase structure of Cr(Pt)+Cr₃Pt can be precipitated
- Cr₃Pt and desired Cr₃PtN perovskite phase have same metal component stoichiometry (3Cr :1Pt)

Two-Phase Cr(Pt)+Cr₃Pt Cr-5Pt at.% Alloy Exhibited In-Place Internal Nitridation

Cross-Section SEM Micrograph of Cr-5Pt at.% Held in High-Purity Nitrogen at 1000°C for 24 h



*EPMA Data Consistent with In-Place Internal Nitridation to Form Cr_3PtN



Cr₂N: 74Cr-26N at. %

Nitrided Cr(Pt) (dark gray): 69Cr-1Pt-30N at. %

Nitrided Cr₃Pt (white): 65Cr-13Pt-22N at. %

Cr(Pt) Metal (light gray): 99Cr-1Pt at. %

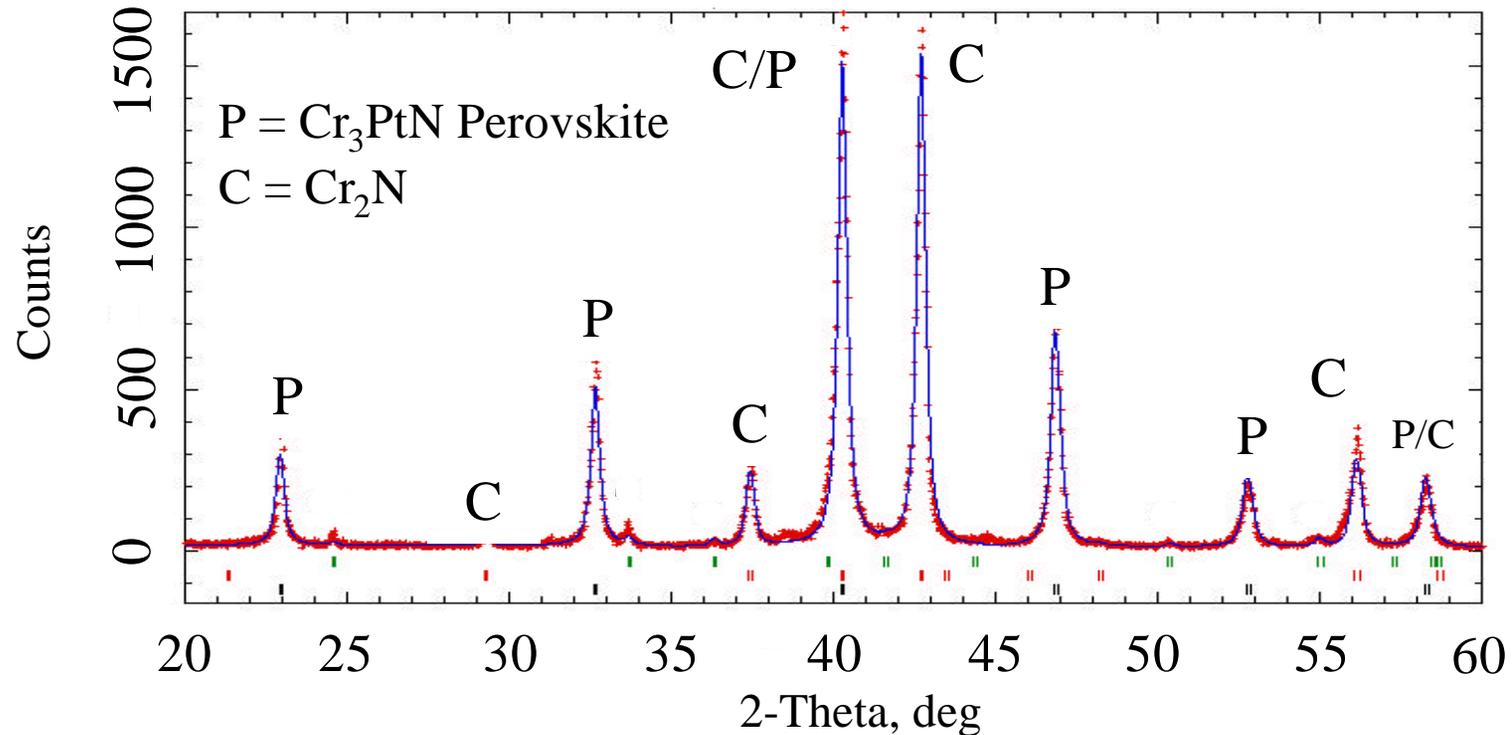
Nitrided Cr₃Pt (white): 69Cr-16Pt-15N at. %

Cr(Pt) Metal: 99Cr-1Pt at. %

Cr₃Pt Metal: 86Cr-14Pt at. %

*Microprobe data semi-quantitative due to small particle size

*Quantitative Rietveld XRD Analysis Confirms Presence of Cr₃PtN Perovskite



- Estimate 64.5 weight fraction Cr₂N, 32.9 weight fraction Cr₃PtN, and 2.6 weight fraction Cr₂O₃ (casting inclusion?)
- Calculated XRD weight fractions for Cr₂N and Cr₃PtN correlate well with estimate of 63 wt.% Cr(Pt) and 37 wt.% Cr₃Pt in the initial alloy structure

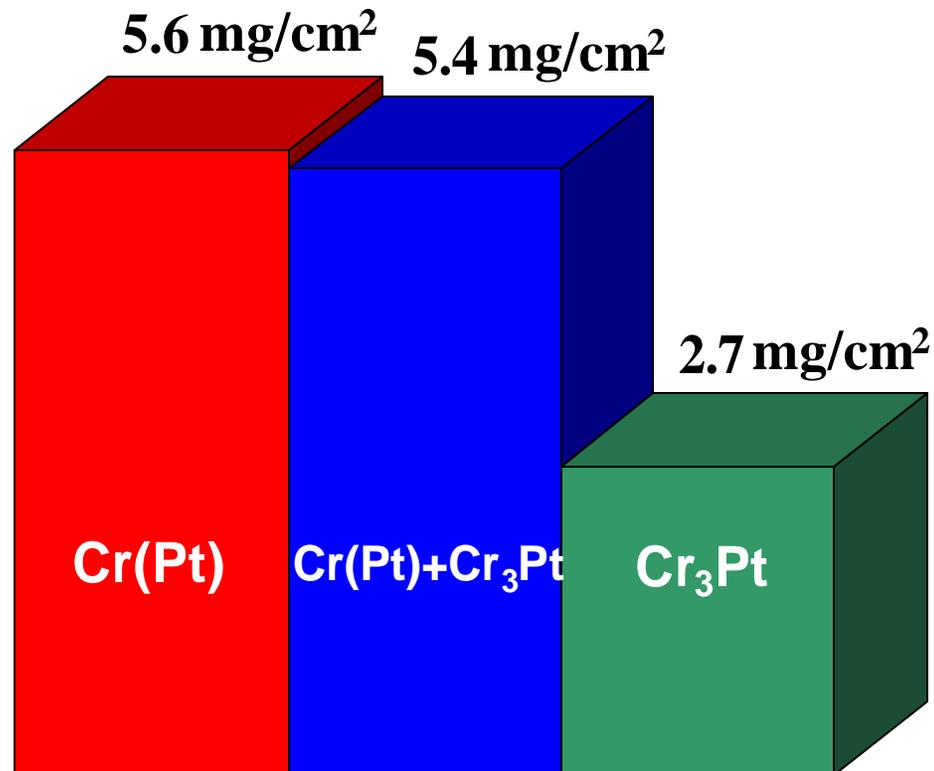
*Cr₂N surface scale removed, structure also analyzed by TEM

Characterization of Nitrided Cr-5Pt at.% Consistent with Formation of Cr₃PtN Perovskite at Cr₃Pt Sites by In-Place Internal Nitridation

- No evidence of Cr₃Pt internally nitriding to form Cr₂N + Pt
- What about mechanistic details?
 - Insight from nitridation of single-phase Cr(Pt) and Cr₃Pt alloys

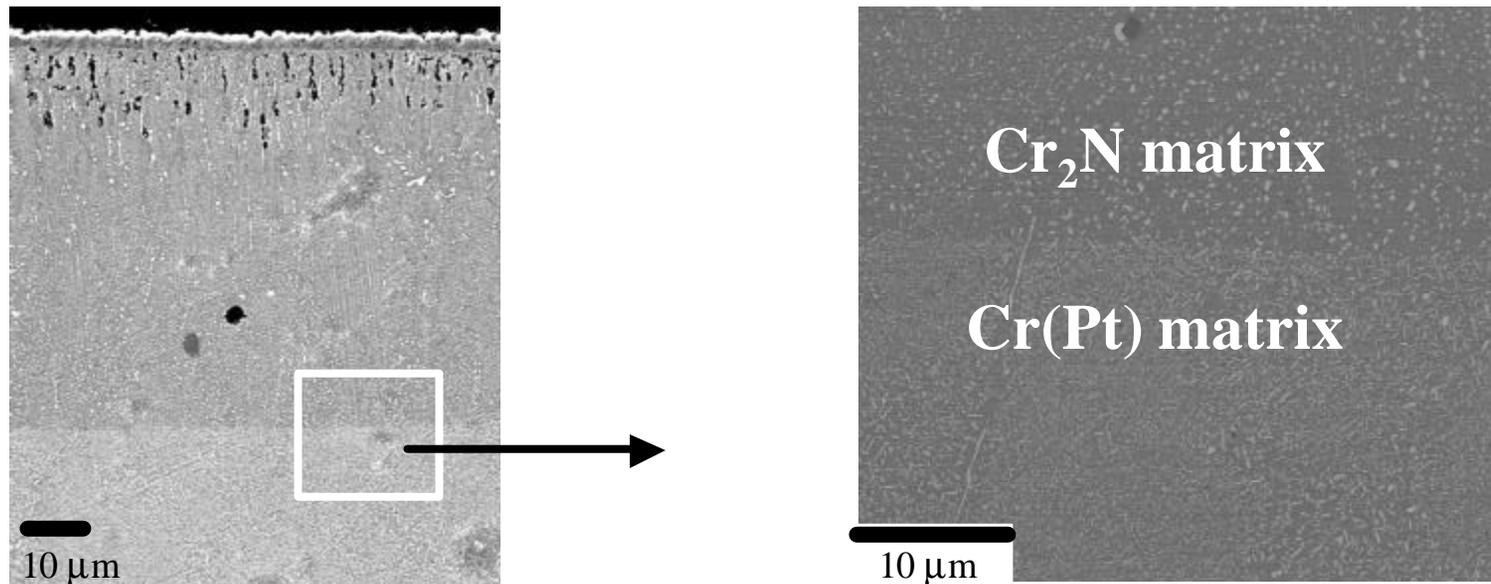
Nitridation Weight Change Data Suggests Two-Phase Cr(Pt)+Cr₃Pt Alloy Behaved Like Single-Phase Cr(Pt) Cr-2.25Pt at.% Alloy

Isothermal Weight Change Data after 24 h at 1000°C in Nitrogen



“Single Phase” Cr(Pt) Alloy Exhibited Similar In-Place Internal Nitridation to Cr-5Pt at.%

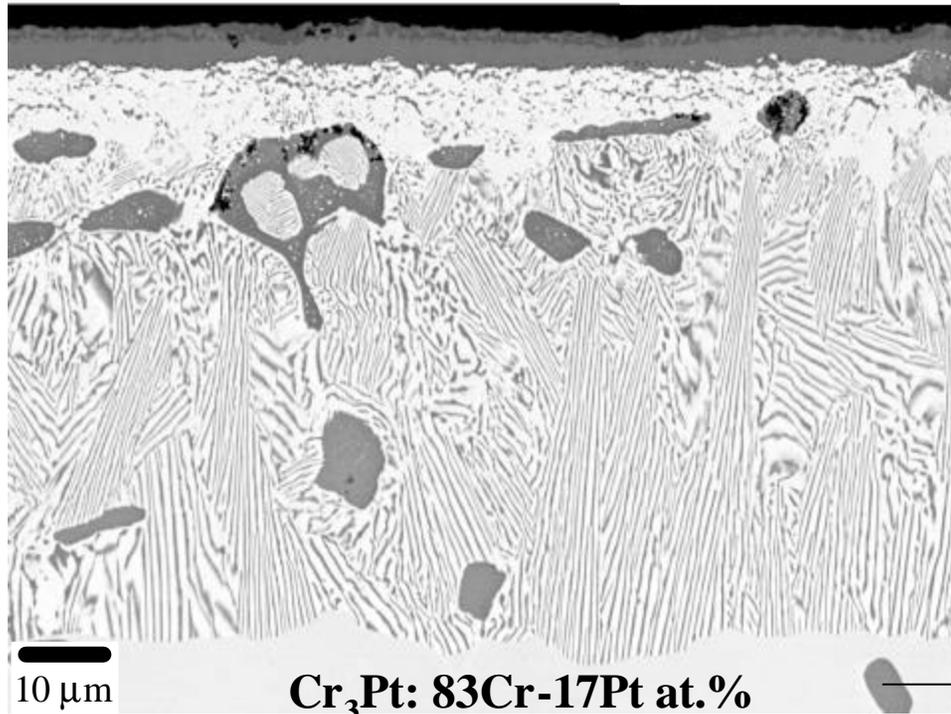
Cross-Section SEM Micrographs of Cr-2.25Pt at.% after 24 h at 1000°C in Nitrogen



- Fine second phase dispersion not yet analyzed (suspect $\text{Cr}_3\text{PtN/Cr}_3\text{Pt}$)

Nitrided “Single-Phase” Cr_3Pt Exhibited Discontinuous-Type Phase Transformation

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



Cr_2N : 70Cr-30N at.%

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

**White lamellar phase:
 Cr_3PtN 65Cr-18Pt-17N at.%**

**Dark lamellar Phase: Cr-rich
 Cr_3Pt 84Cr-13Pt-3N at.%**

**Cr(Pt) Phase:
nominal 99Cr-1Pt at.%**

- Speculate reaction driven by need to eliminate excess Cr to stabilize Cr_3PtN perovskite structure (requires 3Cr:1Pt)
- Cr(Pt) matrix speculated to accommodate excess Cr when Cr_3Pt is present as a second phase dispersion (e.g. Cr-5Pt)

*EPMA composition data semi-quantitative due to fine phase size, phase identification based only on EPMA

Future Work

- Detailed Study of Nitridation in the Cr(Pt)-Cr₃Pt System
 - Single-Phase Cr₃Pt as a function of Cr:Pt ratio
 - Two-Phase Cr(Pt) + Cr₃Pt as a function of vol.%
 - Single-crystal precursor to modify precipitated Cr(Pt)/Cr₃Pt structure (with Ames Lab)

- Attempt to Make Nanoscale Complex Ceramic Dispersions
 - Amorphous parent phase to aid in precipitating nanoscale metallic precipitates
 - Thin-film metallic precursor structure to minimize processing time for oxidation reaction