Materials Design Opportunities From Reactions in Multi-Phase Materials

Michael P. Brady, I.G. Wright, P.F. Tortorelli, C.T. Liu
Oak Ridge National Laboratory
Oak Ridge, TN USA

16th Annual Conference on Fossil Energy Materials
Baltimore, MD, USA
April 24, 2002

Broad Phenomenological Talk

- Not an Existing Program- Collection of Observations Highlighting One Possible Direction for Fossil ARM Effort (examples from Fossil, OTT, NASA, others)

- Bring Attention to Potential Utility of Overlooked Phenomena Related to Oxidation Reactions in **Multi-Phase** Alloys as a Basis for Breakthrough Materials and Processes

- Strategies to Control Alloy Reaction Products
  - -Establishment of protective oxide layers
  - -Management of embrittling species
  - -Synthesis of functional surfaces (fuel cells, magnetic media)

Why a Talk Like This?

To Achieve Many Targeted Technological Goals, Including Vision 21,
We Will Require New Materials Design Approaches and Processes

Manipulation of Multi-Phase Phenomena as a Basis for Materials Design

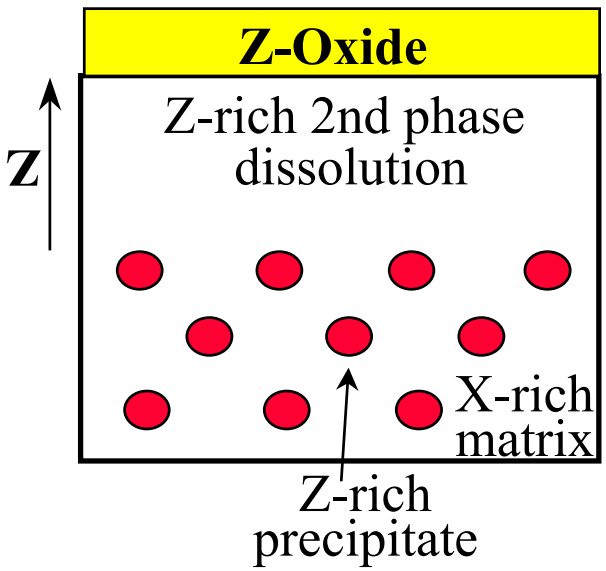
- Greater Opportunity to Co-Optimize Mechanical Properties for Ambient- and High- Temperatures
  - Toughening: ductile particles, interphase interfaces
  - Strengthening: precipitate phases, oxide dispersions

- Multi-Phase Generally Viewed as Detrimental to Protective Oxide Layer Formation to Resist Corrosion
  - **NOT ALWAYS THE CASE!**
  - Leverage thermodynamic and kinetic degrees of freedom not available in single-phase systems

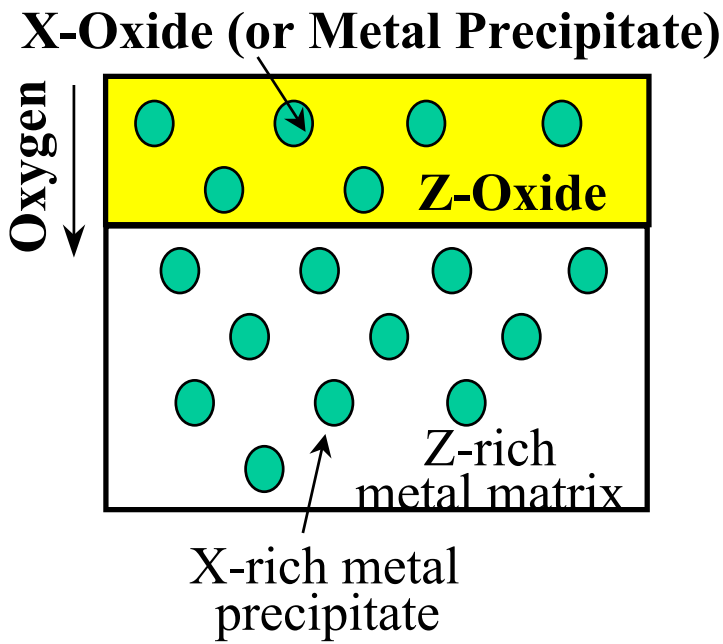
Oxidation Reactions in Multi-Phase Alloys Yield an Incredible Range of Surfaces

Two Limiting Cases

Cooperative Mode



Independent (In-Place)



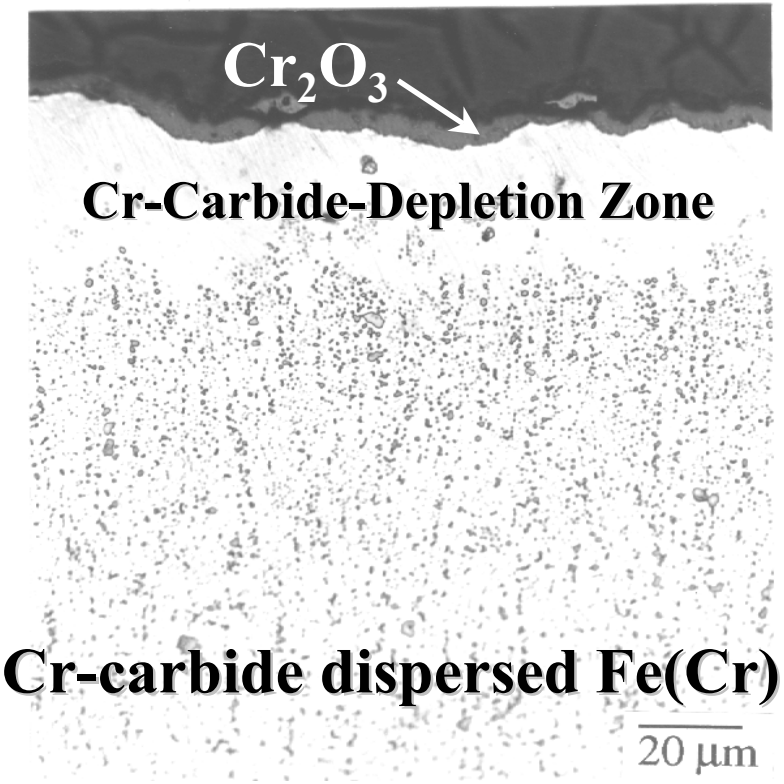
- Cooperative: Single-Phase Reaction Product
- Independent (In-Place): Composite Surface Which Mimics Underlying Alloy Structure

Present a Series of Phenomenological/Microstructural Examples Illustrating How Cooperative and Independent Reaction Modes Can be Manipulated to Produce Interesting and Potential Useful Results

Establishment of Protective Oxide Layers

Protective Oxide Layer by Reservoir Effect

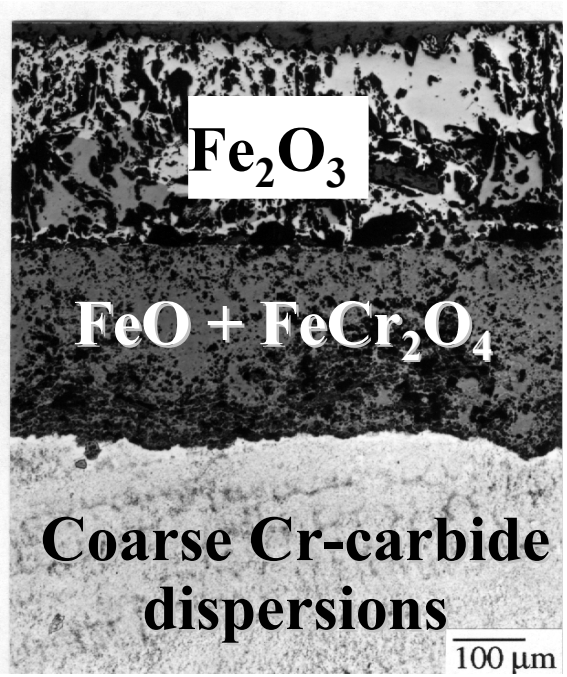
Light microscopy cross-section of Fe-15Cr-0.5C wt.% after 72 h at 850°C in oxygen (Durham, Gleeson, Young 1998)



- Cr-carbides provide strengthening
- Classic example of cooperative oxidation

Microstructure Important

Light microscopy cross-section of **as-cast** Fe-15Cr-0.5C wt.%
After 72 h at 850°C in oxygen (Durham, Gleeson, Young 1998)

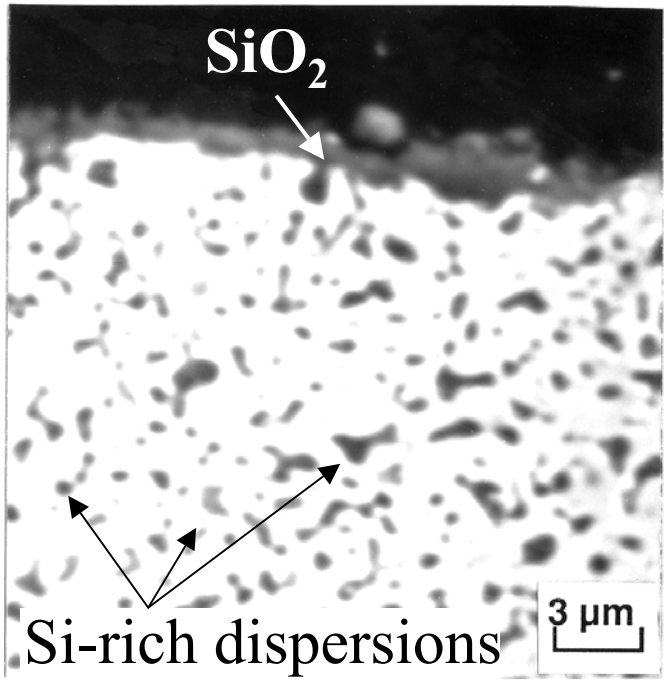


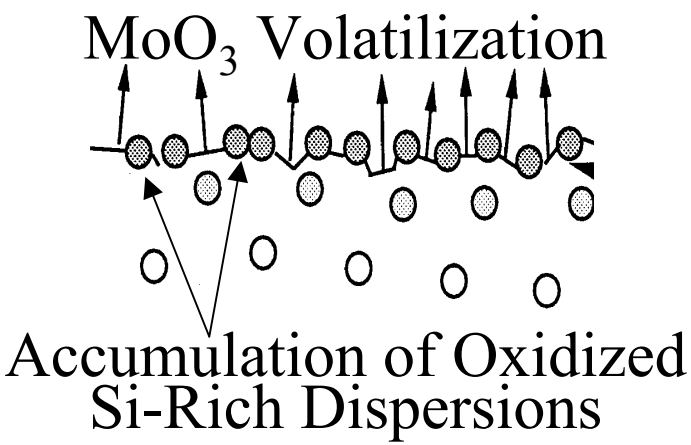
- Cr tied up in coarse, poorly distributed carbides which results in formation of less-protective Fe-oxides rather than Cr_2O_3
- Partitioning of Cr among two phases neutral (microstructure optimized) or detrimental to oxidation

Dispersed Reservoir Concept- Addition of Dispersoids to Create a Reservoir Effect

(Wright, Nagarajan, Stringer, et al. 1980's-early 90's)

SEM Cross-section of Mo-6Si-15Si_3N_4 wt.%: 1000°C,111h,Air





- Mo matrix and Si_3N_4 dispersions oxidize independently to yield a SiO_2 layer by matrix recession/particle accumulation

Won’t Artificial Dispersoids Degrade Mechanical Properties?

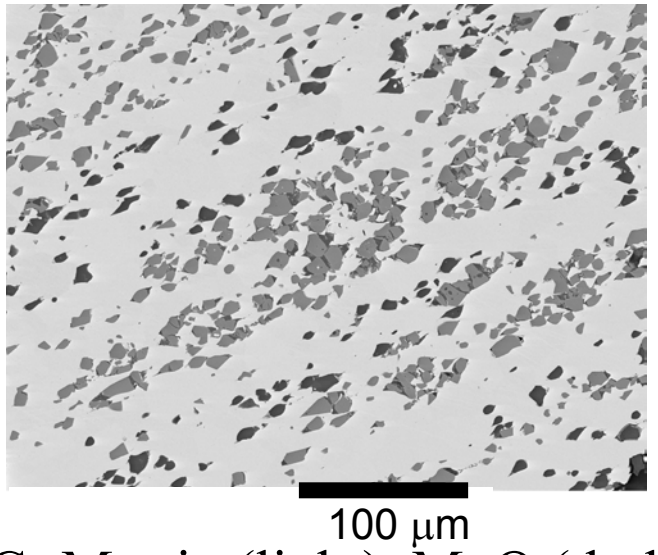
- Not Necessarily!
- Can be Beneficial- e.g. BCC Refractory Metals

Additions of MgO Ductilize Cr at Room-Temperature

(Scruggs, early 1960's)

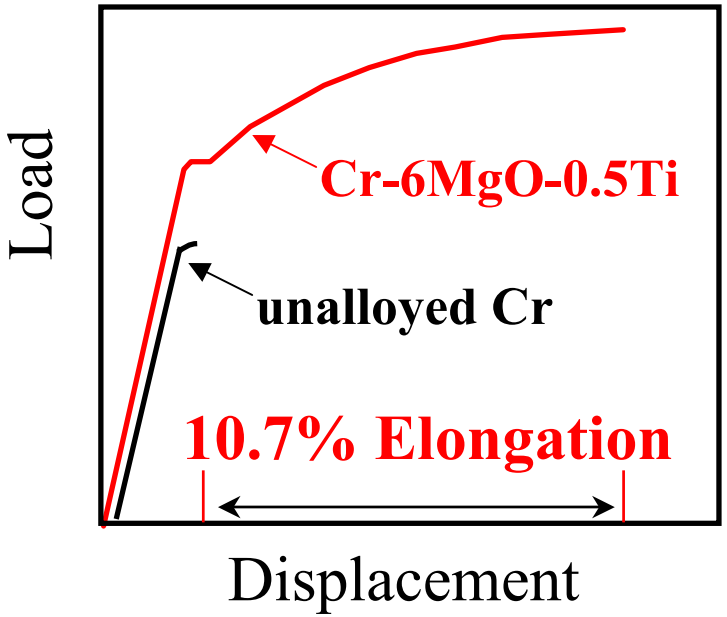
Cr-6MgO-0.5Ti wt.%

Microstructure (SEM)



Cr Matrix (light), MgO (dark)
$MgCr_2O_4$ Spinel (gray)

Tensile Behavior



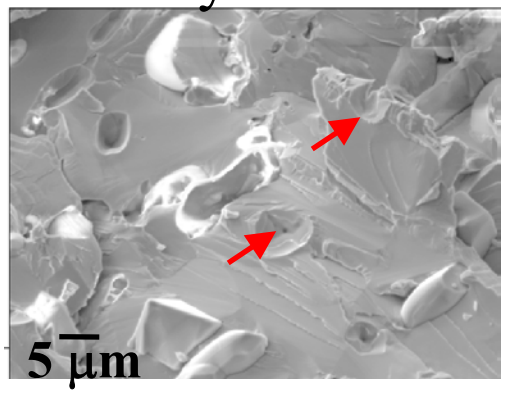
- Similar improvements in mechanical properties reported for oxide-dispersed Mo

Deleterious Tramp Impurities Segregate to Cr/Oxide-Dispersion Interfaces

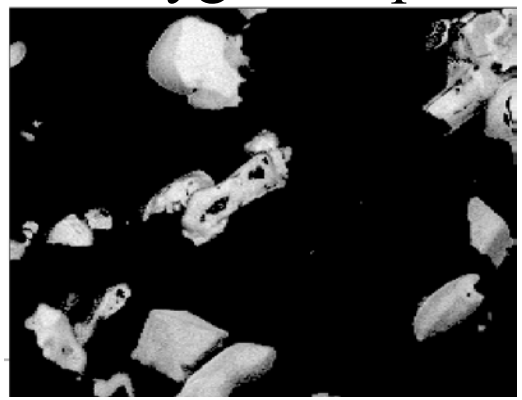
Auger Maps of In-Situ Fractured Cr-6MgO-0.5Ti

(*Ti peak overlap issues)

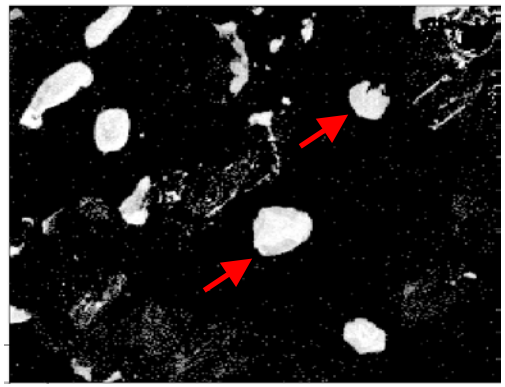
Secondary Mode SEM



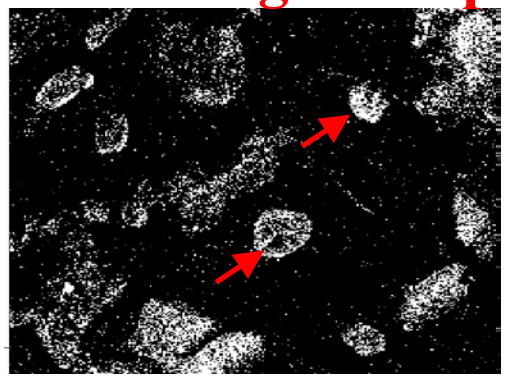
Oxygen Map



Sulfur Map

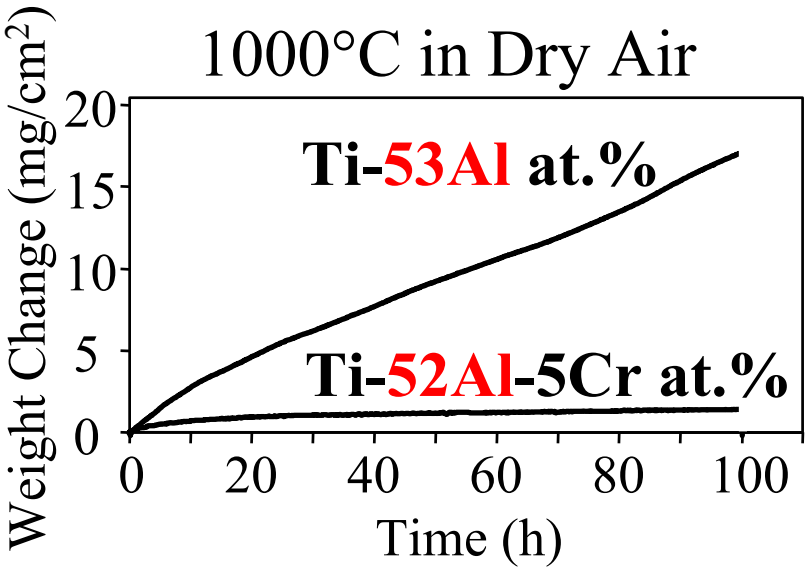


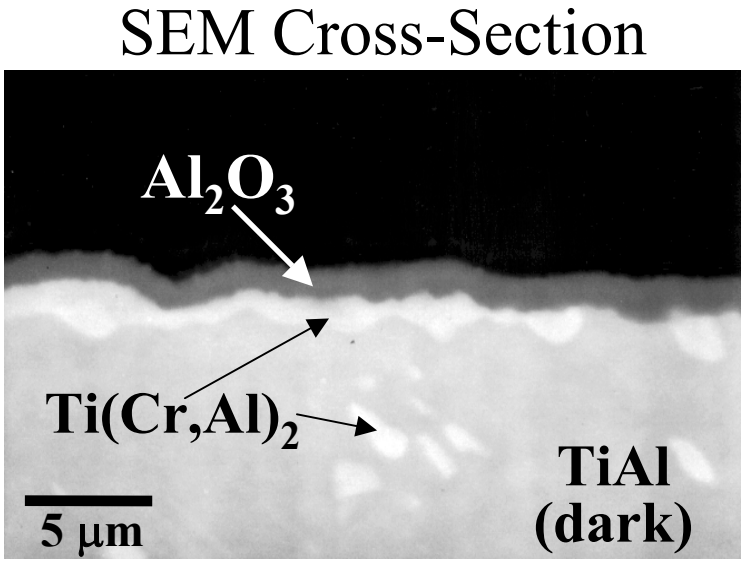
***Nitrogen Map**



- Cleans up Cr Grain Boundaries (other effects also important)

Alloying to Create a Cooperative Reservoir Effect



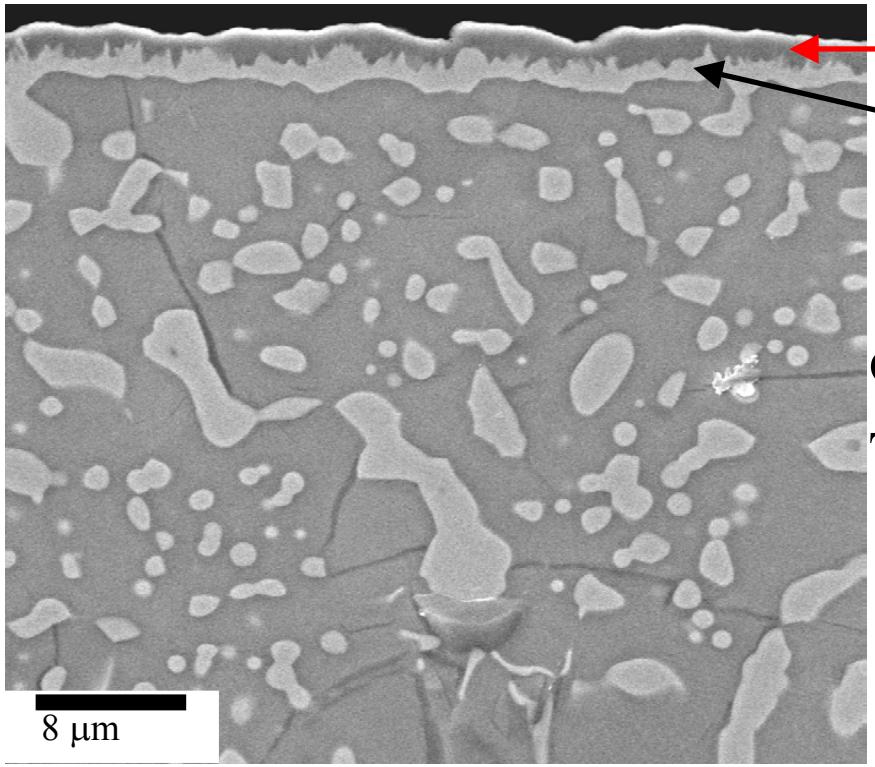


- Not secondary gettering-Cr more noble in oxygen than Ti,Al
- Cr enrichment at alloy/scale interface shifts Al depletion path towards $Ti(Cr,Al)_2$ phase field-keeps less oxidation-resistant Ti_3Al and related phases from forming (cooperative effect)
- Works for other **noble alloying additions** in Ti-Al (e.g. Fe, Cu,Quadakkers et al. Ag effect)

Management of Interstitial Dissolution and/or Embrittlement

Nitrogen Penetration Limited by Ti_2Ni Formation at Alloy/Scale Interface

SEM Cross-Section of Ti-10Ni at.%: 24 h, 50°C, N_2-$4H_2$



External Ti-Nitride layer

Ti_2Ni layer (light)

α–Ti Matrix (dark)

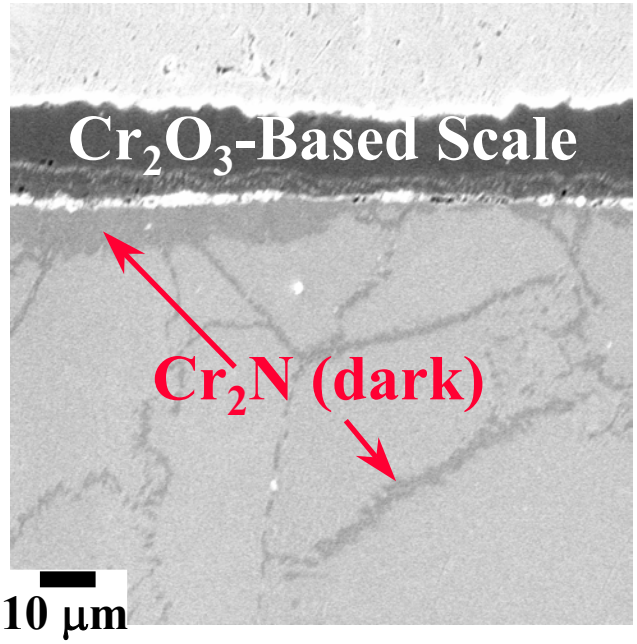
Ti_2Ni second phase(light)

- Pure Ti exhibits nitrogen dissolution under external Ti-nitride
- Ni enrichment (noble)/cooperative reaction results in Ti_2Ni nitrogen dissolution barrier under external Ti-nitride

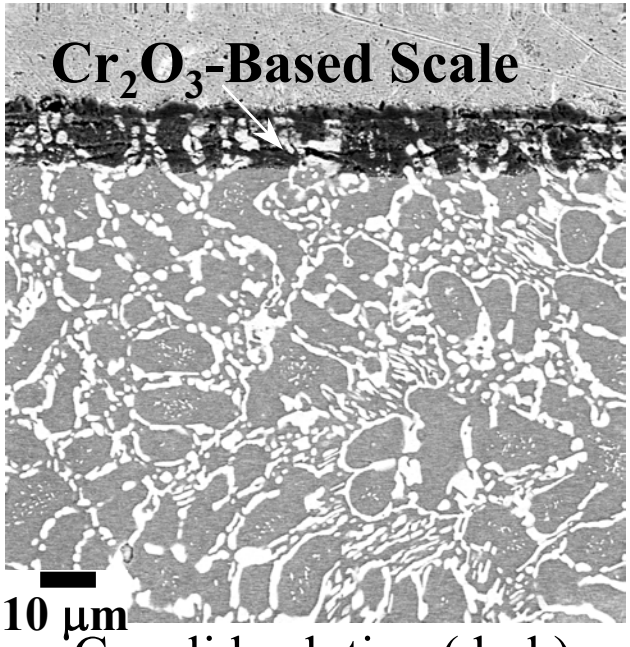
Cr_2N Subscale Formation Hindered When Cr_2Ta Laves Phase Present as Second Phase

SEM Cross-Sections After 1000 h at 900ºC in Air

Single-Phase Cr Solid Solution
Cr-**1Ta**-5Mo-0.2La at.%



Cr_2Ta Laves Phase Reinforced
Cr-**8Ta**-5Mo-0.2La at.%



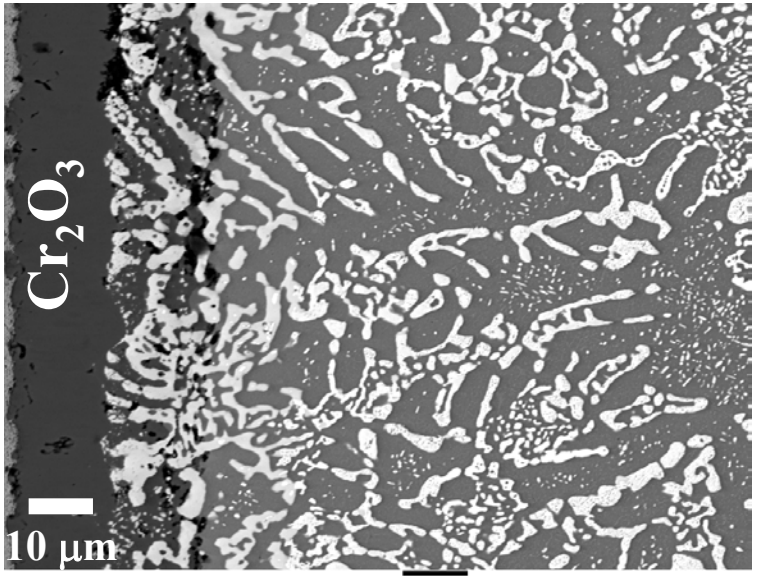
Cr solid solution (dark)
Cr_2Ta Laves Phase (light)

- Cr_2N subscale formation/grain boundary penetration embrittles Cr

In-Place Internal Nitridation of Cr_2Ta Laves Phase Getters Nitrogen

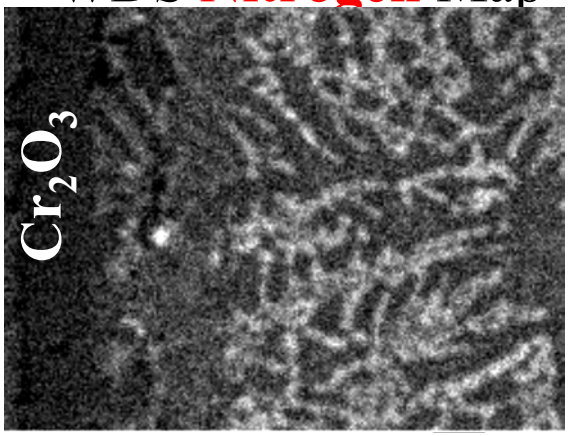
Cr-9.5Ta at.% After 120 h at 1100°C in Air

SEM Backscatter Mode

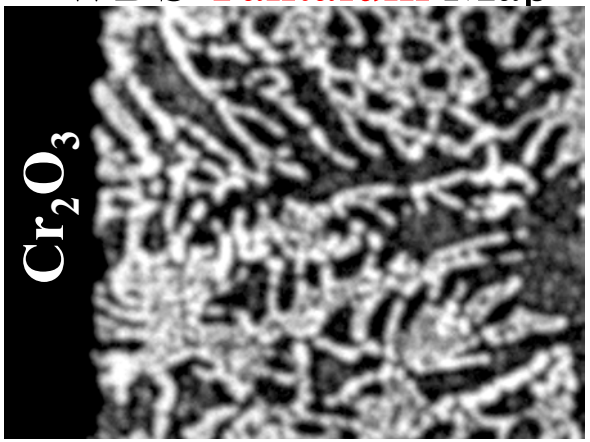


Cr_2Ta Laves Phase (light)
Cr solid solution (dark)

WDS Nitrogen Map



WDS Tantalum Map



- Keeps nitrogen from embrittling Cr matrix phase

Manipulation of $Cr\text{-}Cr_2Ta$ to Improve Room-Temperature Fracture Toughness

$Cr\text{-}Cr_2Ta$ Eutectic	Fracture Toughness ($MPa\ m^{1/2}$)
Binary	**8-10**
Microalloyed	**12-14**
Macroalloyed	**20-21**

- Alloying addition site occupancy, phase partitioning, eutectic composition/microstructure all key

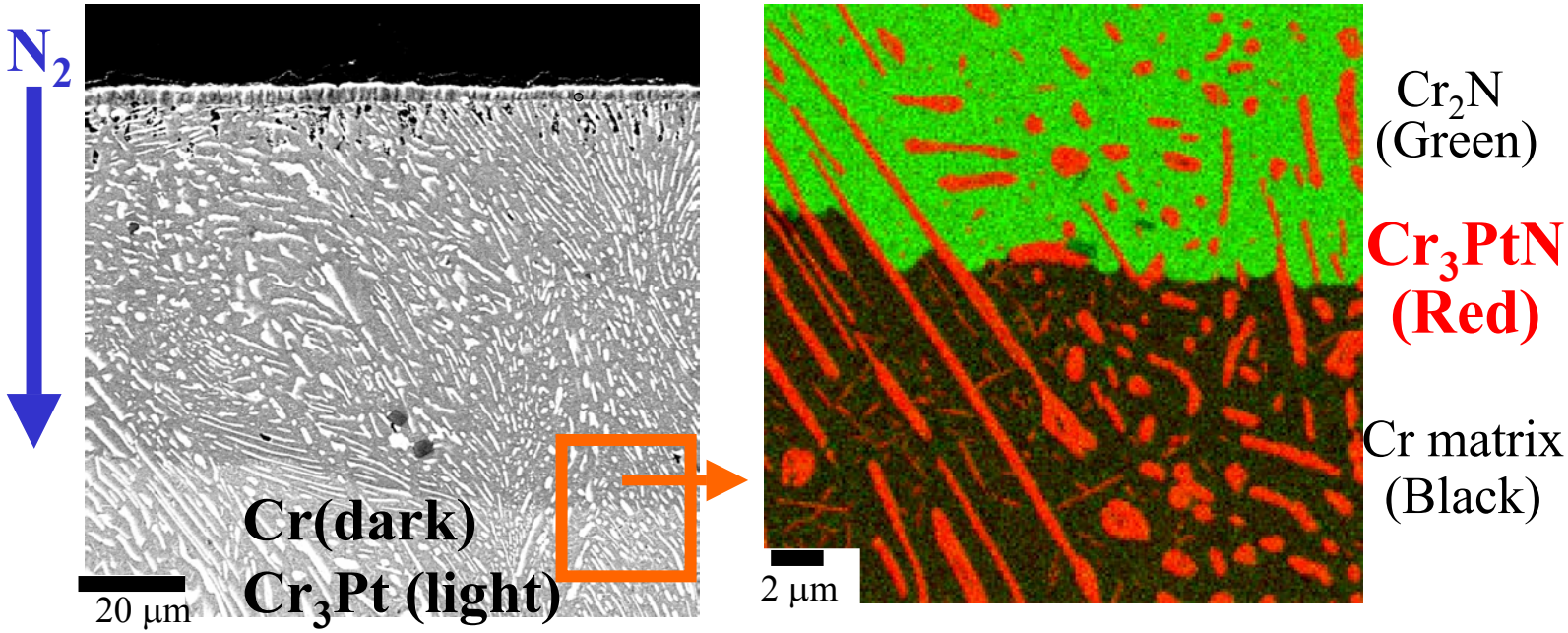
Synthesis of Functional Surfaces

Independent Reaction Mode: Use Underlying Alloy Structure as a Template

Nitridation of Model Cr_3Pt-Dispersed Cr Alloy

SEM Cross-Section

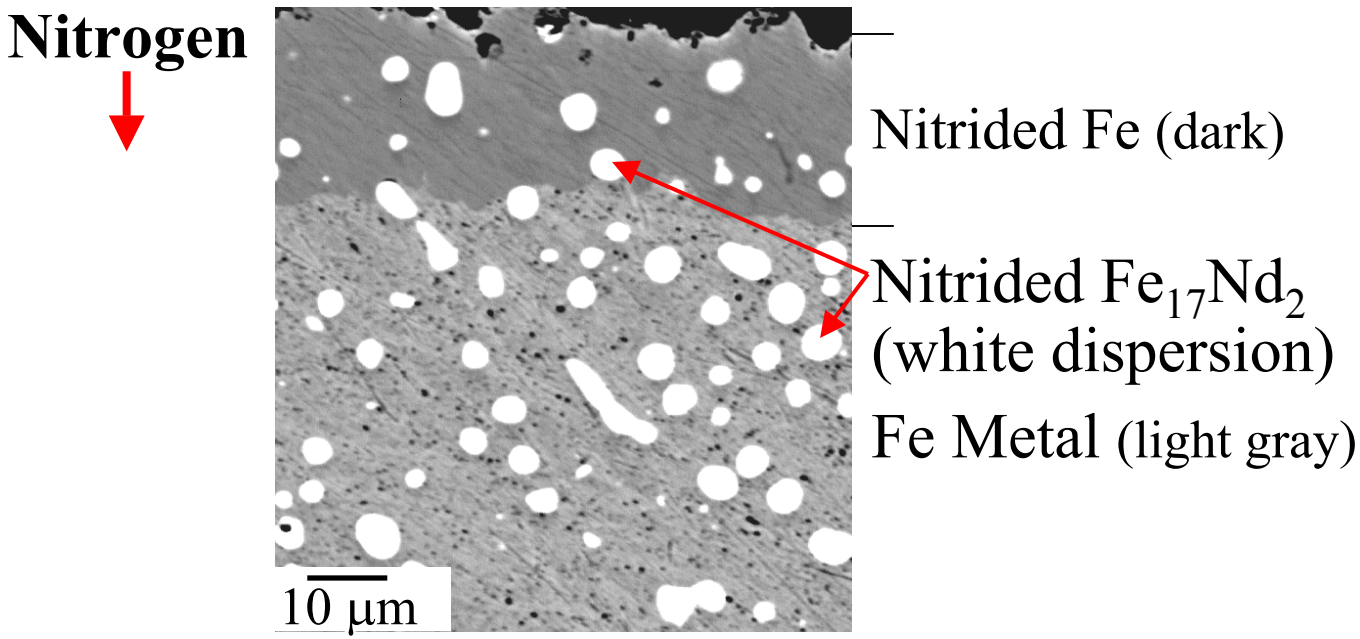
Spectrum Image Phase Map



- Formation of Cr_3PtN Perovskite at Cr_3Pt phase regions
- Controlled synthesis of complex ceramic phase dispersion

Independent Mode Nitridation of $Fe_{17}Nd_2$ Dispersed Fe for Magnetic Applications

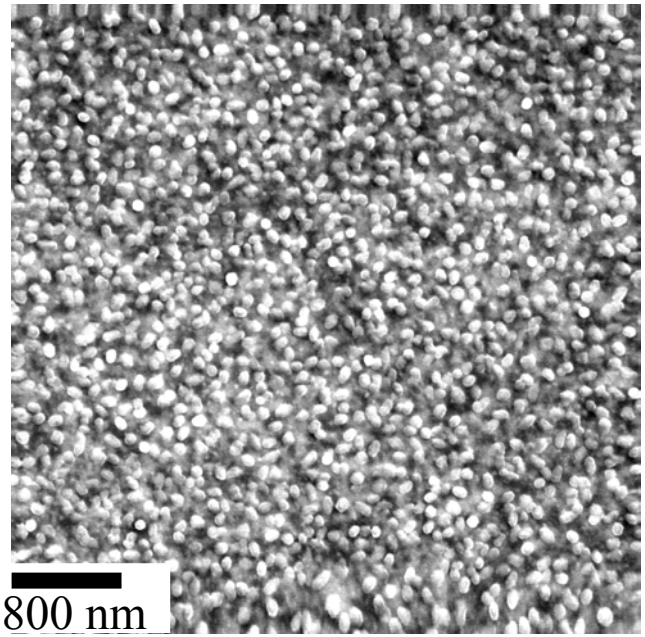
SEM Cross-Section of Nitrided 99Fe-1Nd at.%



- Coarse structure derived from arc-cast/annealed material (try non-equilibrium processing to get nano metal precipitates)
- Goal is hard magnetic intermetallic nitride nanodispersions in hard/soft/non magnetic simple ceramic or metallic matrices

In-Situ Cermet Formation by Independent Mode Oxidation of Si-Ag Thin Film

SEM Surface of Si-Ag Thin Film After Oxidation
(Si and Ag immiscible)



Ag "Balls" (light)

SiO_2 Matrix (dark)

- Mechanism likely also involves Ag outward diffusion
- Potential solid oxide fuel cell metal interconnect coating???
  - -SiO_2 for oxidation protection
  - -Through thickness Ag for electrical contact

Reactions in Multi-Phase Structures Provide Opportunities for Breakthrough Materials Development

- Many details, subtleties broadbrushed
  - -Happy to discuss specifics of all examples given

- Point is: Reactions in multi-phase systems involve spectacular range of interesting and **potentially** useful phenomena unattainable using conventional approaches
  - -Worthy of consideration and further study