Consolidation of Gas Atomized Precursor Alloy Powder for the Formation of an Oxide Dispersion Strengthened Ferritic Stainless Steel Microstructure

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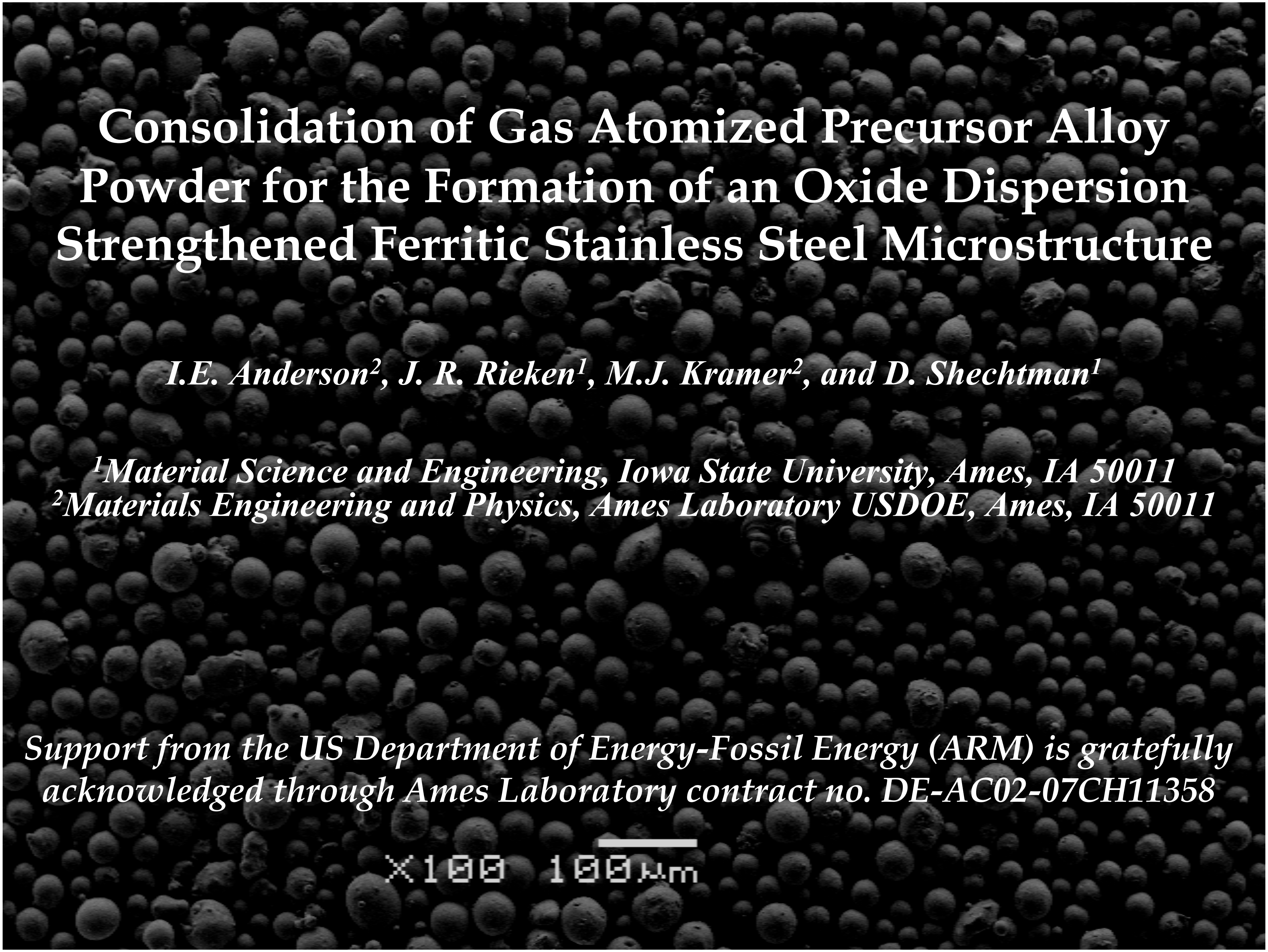

Introduction-Future Applications

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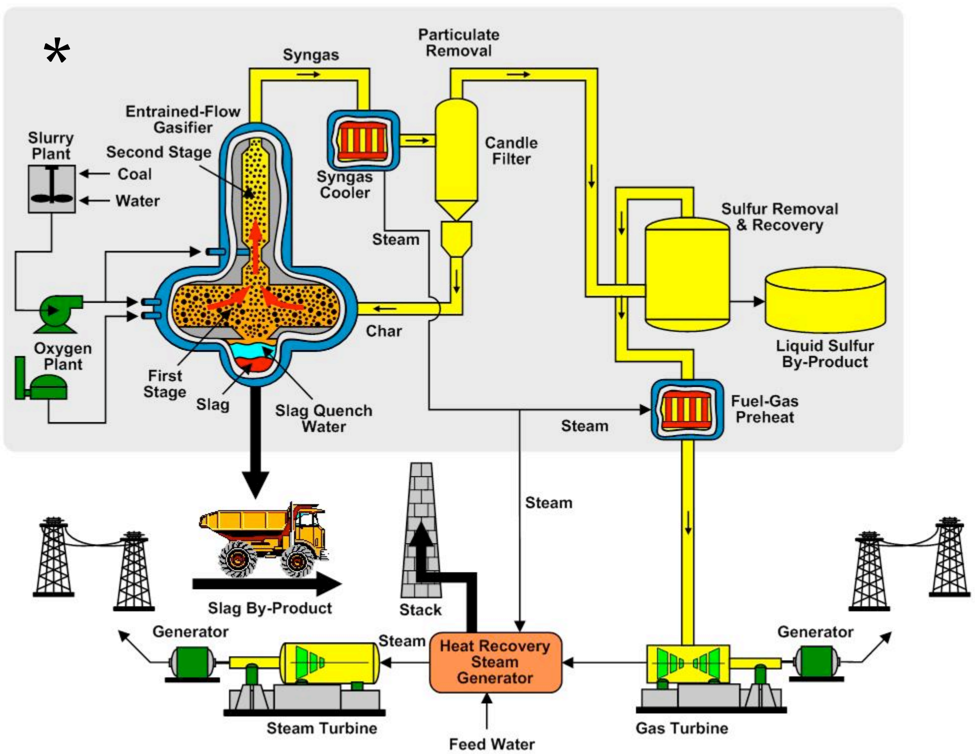

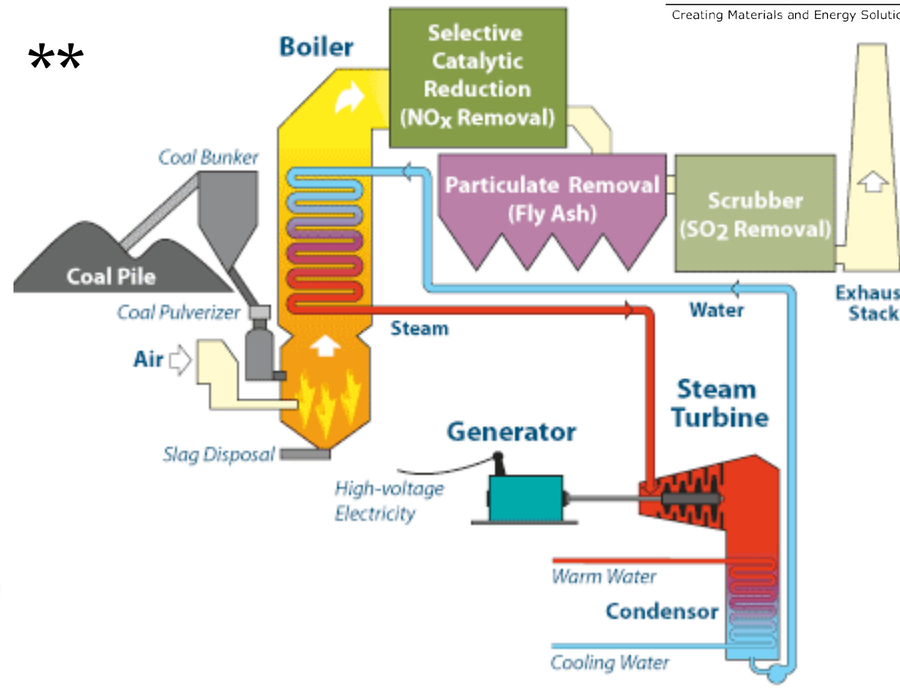

***Coal Gasification Plants:**

- **Heat Exchanger tubing**
- **Combustion wall material**
- **Burner hardware**

****USC Steam Coal Fired Plants:**

- **Boiler materials**
- **Heat exchanger tubing**
- **Exhaust liner materials**

Inherent Properties:

- **Good thermal conductivity**
- **Low thermal expansion**
- **Cost effective**
- **Strength loss above 600^{o}C**

 *Source: www.netl.doe.gov **Source: knol.google.com/…/supercriticalpowerplant.gif

Motivation

Mechanical Alloying:

- A high energy mixing process that introduces a base metal, alloying additions, and nonmetal powders (dispersoid element) in a high-energy mill (t > 48 hours)
- *Hot deformation consolidation leads to an anisotropic microstructure and anisotropic mechanical properties (limits applications)

** *Practical developments of NFAs and other nanodispersion-stengthened iron-based alloys poses some significant challenges, including*

➢ *the high cost of mechanically alloyed, powder-consolidated materials compared wi*

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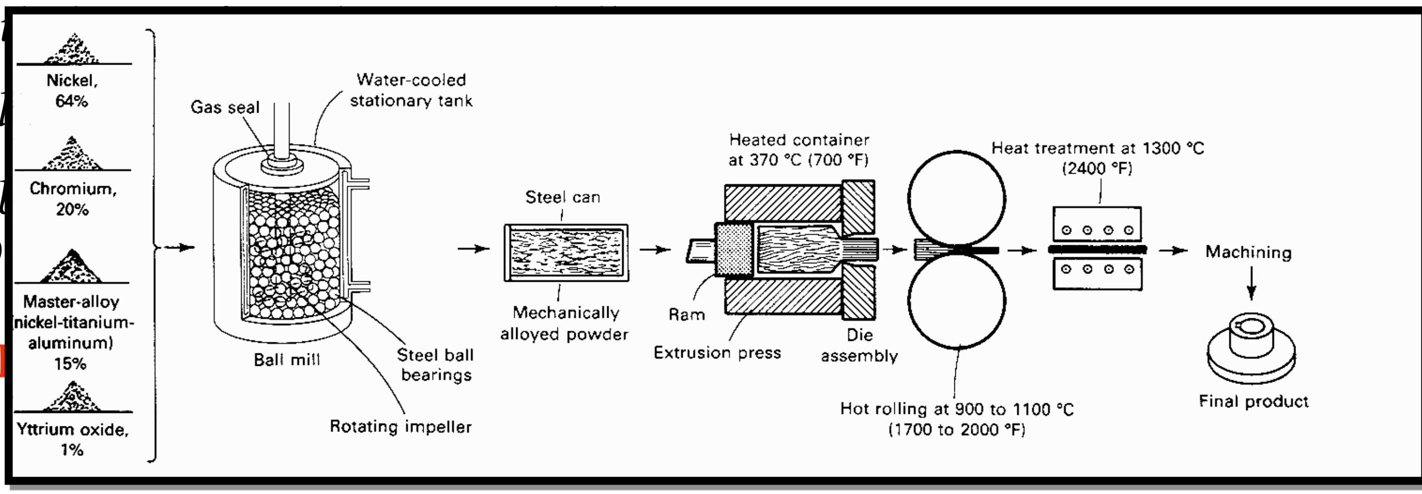

*J.D. Whittenberger et al. , Met Trans A 12A (1981) 845-851

**G.R. Odette, M.J. Alinger, and B.D. Wirth, *Recent Developments in Irradiation-Recent Steels*, Annu. Rev. Mater. Res. 2008. 38:471-503.

Processing Comparison

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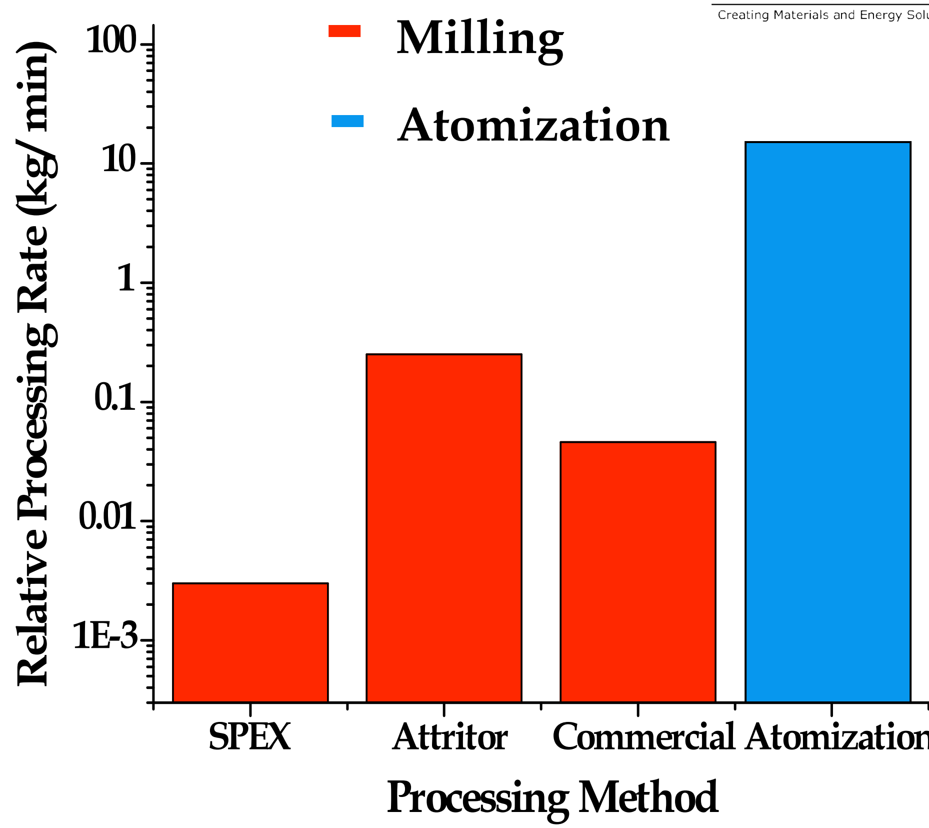
Mechanical Alloying (Milling)

- Long milling times
- Batch commercial process (≈ 200 kg)
- Powder contamination (carbon and milling debris)
- Anisotropic microstructure

Gas Atomization

- Higher processing rates (capabilities of up to 10 kg/min)
- Continuous processing capacity
- Minimized contamination
- Isotropic microstructure
- Rapid solidification benefits



The powder processing rate using gas atomization can be an order of magnitude higher than that of mechanical milling

*C. Suryanarayana, ASM Handbook, Vo. 7, ASM International, Materials Park, OH, 1998, pp. 80-90.

**R.M. German, *Powder Metallurgy and Particulate Materials Processing*, 2005, MPIF, Princeton, NJ.

Goal: Simplify the Manufacturing Process

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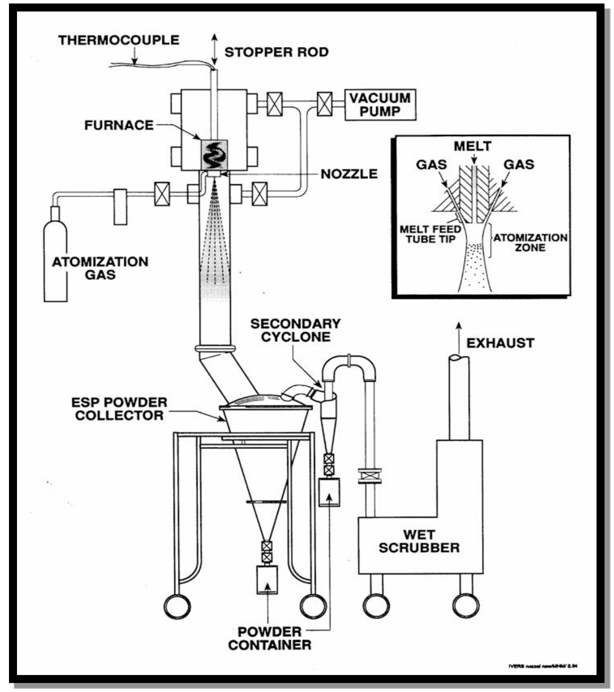
Precursor Atomized Powder, Consolidation, and Heat Treatment:

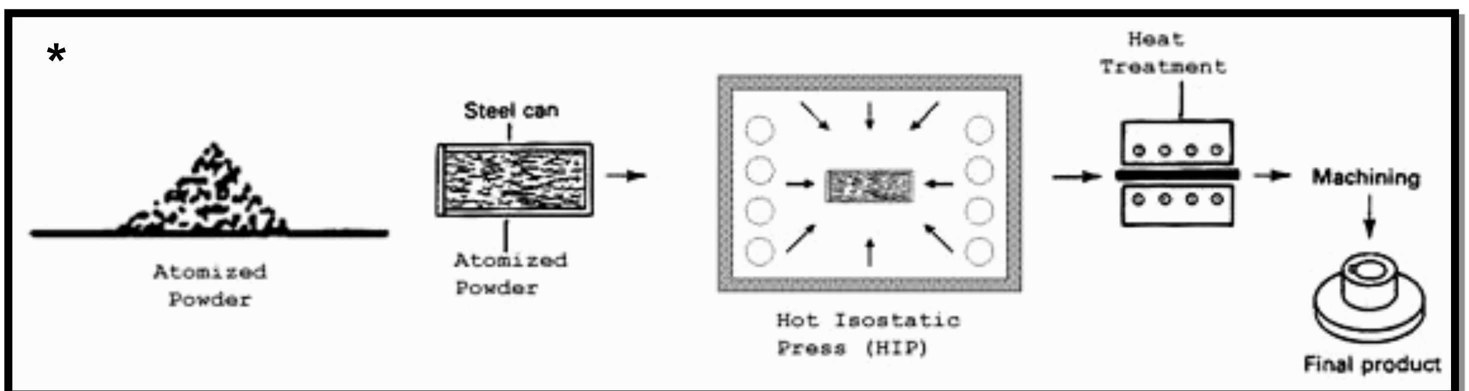
[1] Gas atomization reaction synthesis (GARS) using $Ar\text{-}O_2$ gas mixtures

[2] Hot isostatically pressed retaining an equiaxed grain structure and isotropic mechanical properties

[3] Heat treated to assist further formation of dispersoid phase

Eliminates mechanical alloying and directional deformation processing





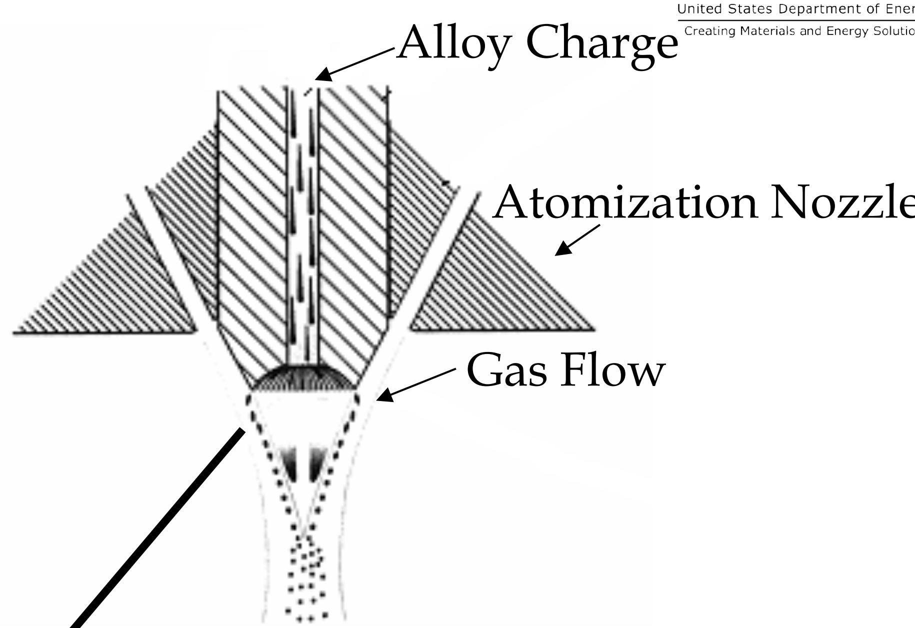
* Terpstra, R.L, Simplified powder processing of oxide dispersion stainless steel, Advances in Powder Metallurgy and Particulate Materials, 2006.

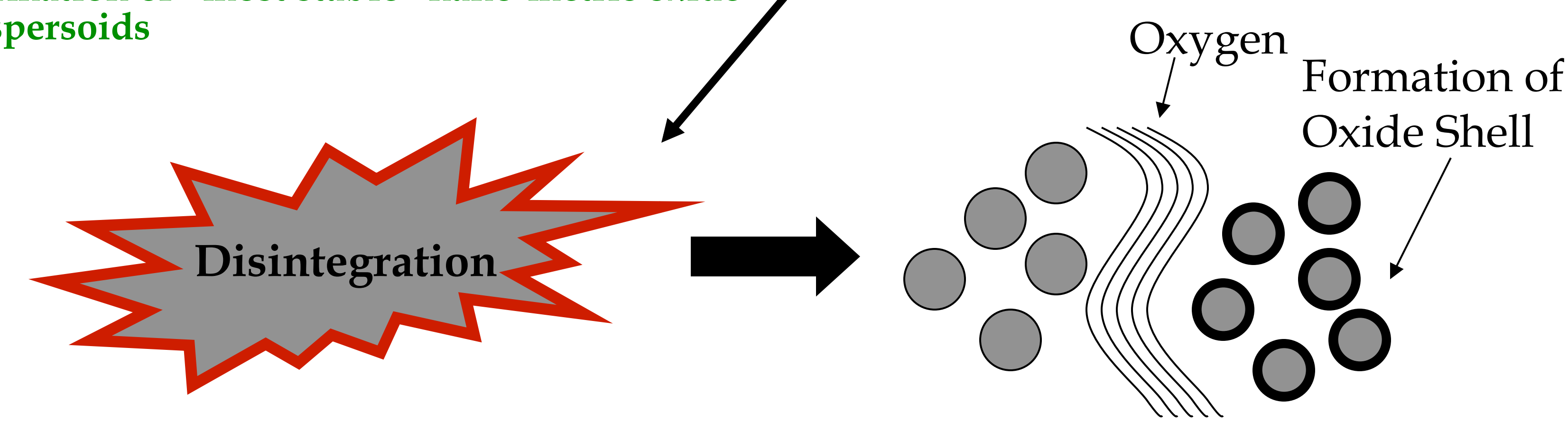
New Precursor Powder Processing

Alloy Design Considerations:
- **Reactive surface oxidation element (e.g., Fe,Cr)**
- **Oxide dispersion forming element (e.g., Y)**

Atomization:
- **Rapid Solidification Process (solute trapping)**
- **Reactive atomization gas (Ar-O_2)**
- **In situ oxidation of the most kinetically favored oxide former**

Consolidation and Heat Treatment:
- **Oxygen exchange reaction (PPB Oxide Dissociation + Yttrium → Dispersoid Formation)**
- **Formation of "most stable" nano-metric oxide dispersoids**





Oxygen Exchange Reaction

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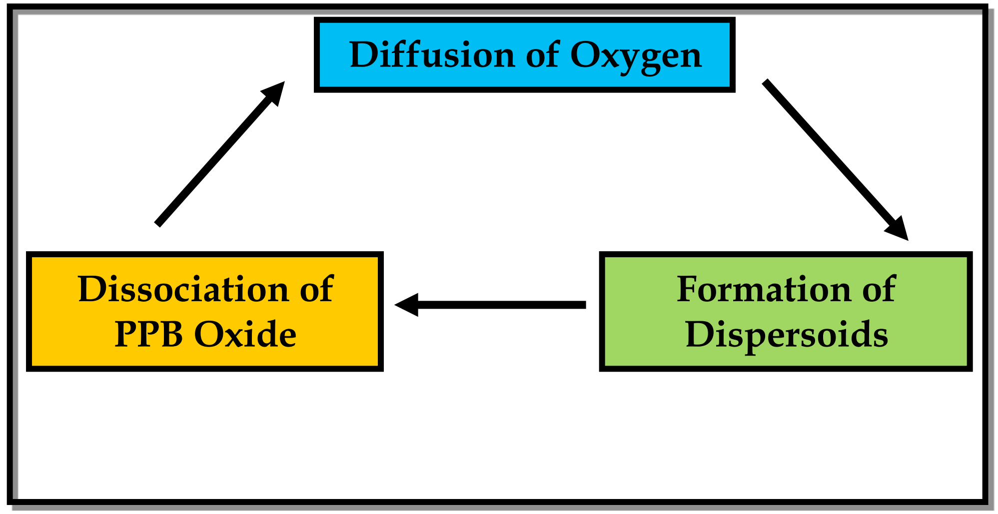
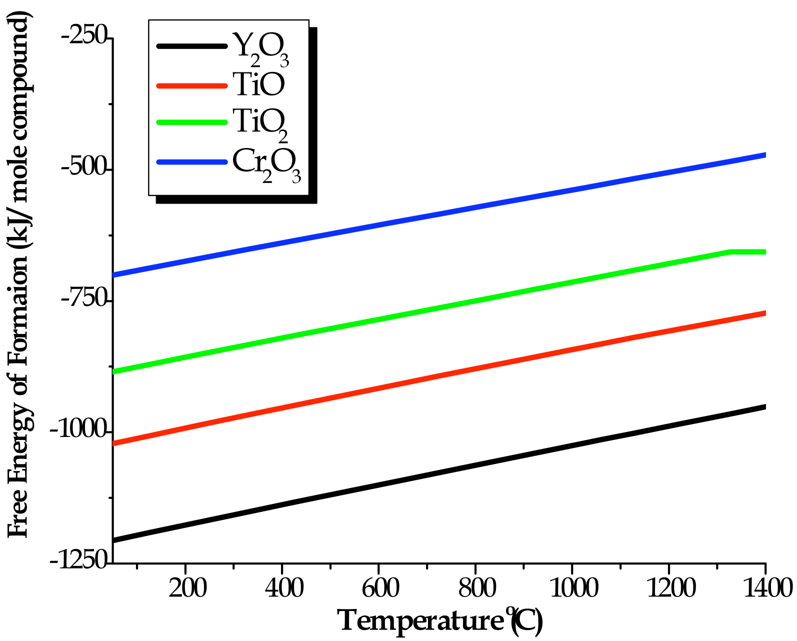
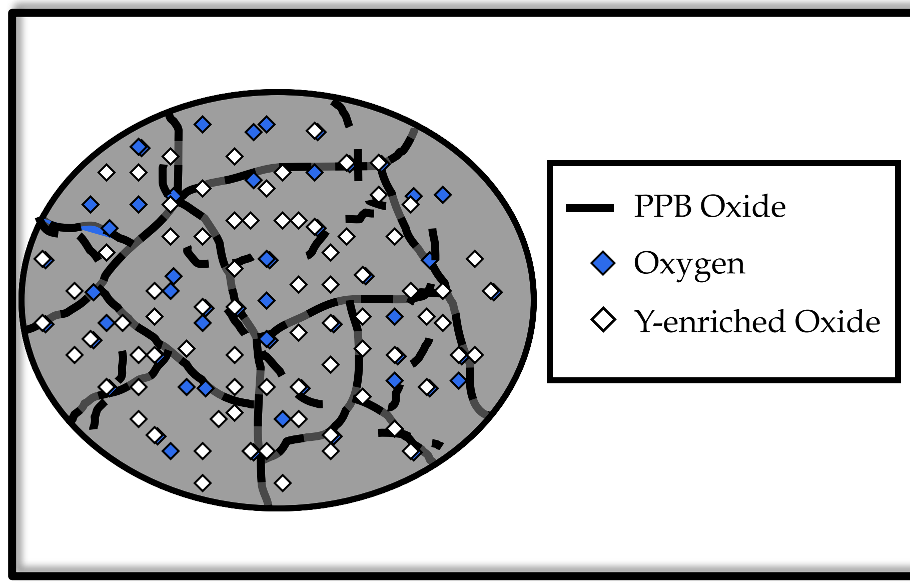
Dispersoid Formation Theory

- PPB oxide dissociation
- Oxygen diffusion
- Nano-metric yttrium-enriched oxide formation

Full dissociation of PPB oxide will be necessary for ideal properties







* Sauert F., Schultze-Rhonhof E., Sheng W.S., Thermochemical Data of Pure Substances, 2nd Edition 1992.

Alloy Development

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Alloy Design (nominal composition)

- **CR-112: Fe-15.0Cr-0.5Y (wt%)**
- **CR-118Ti: Fe-15.0Cr-0.5Y-0.54Ti (wt.%) → addition of Ti**
- **CR-126TiW: Fe-15.0Cr-0.5Y-0.54Ti-3.0W (wt.%) → addition of W**

Actual Chemical Composition

Alloy	Fe (wt.%)	Cr (wt.%)	Y (wt.%)	Ti (wt.%)	W (wt.%)	O (wt.%)	Gas (vol.%)
CR-112	Bal.	14.72	0.15	-	-	0.32	Ar-0.5O_2
CR-118	Bal.	14.90	0.32	0.43	-	0.34	Ar-0.5O_2
CR-126	Bal	14.00	0.15	0.48	2.95	0.16	Ar-0.25O_2

Results

- Microstructure evolution
  - ➢ Can this new simplified processing technique be demonstrated?
- Mechanical Properties
  - ➢ Can these alloys approach the high temperature mechanical properties of commercial Fe-based ODS alloys?

CR-112 Microstructure *(0.09 Y and 1.1 O at.%)*

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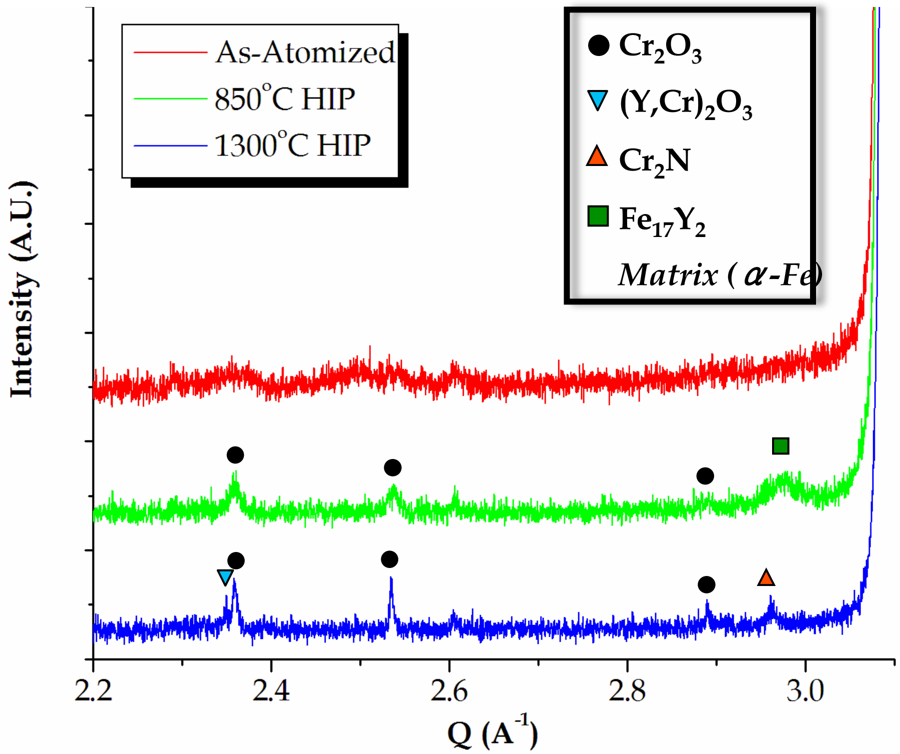
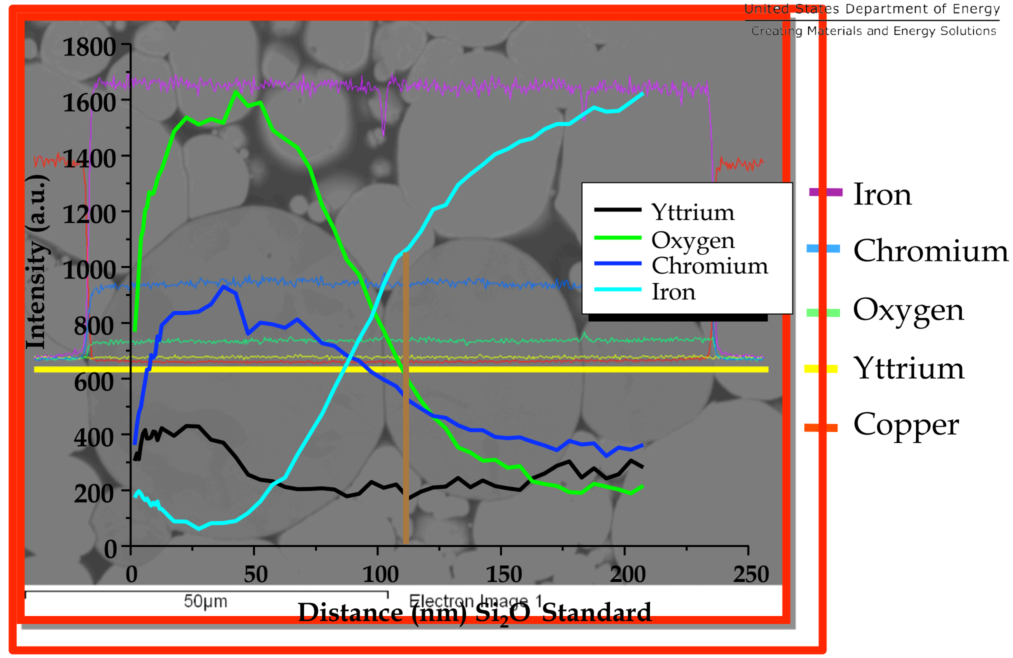
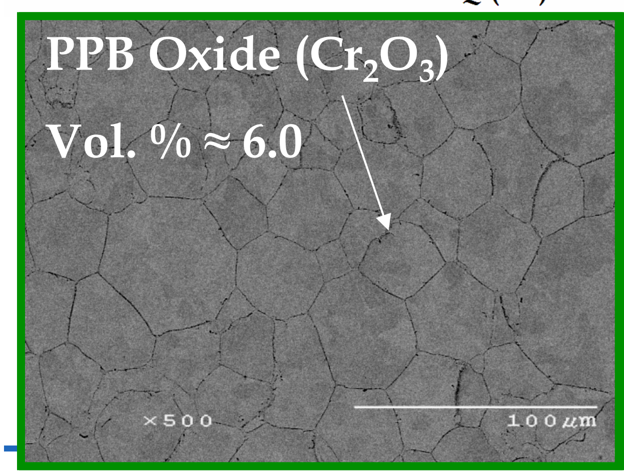
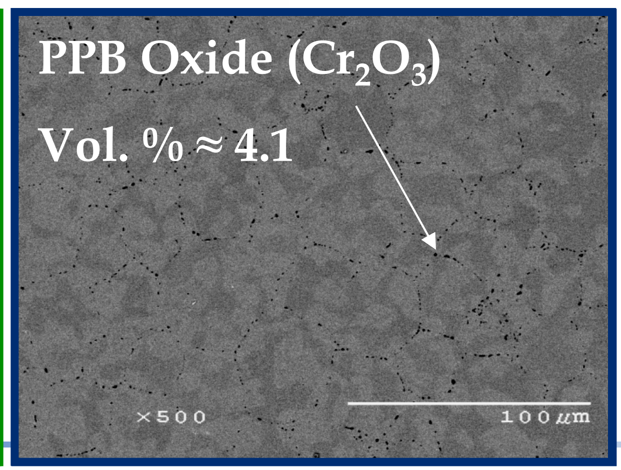


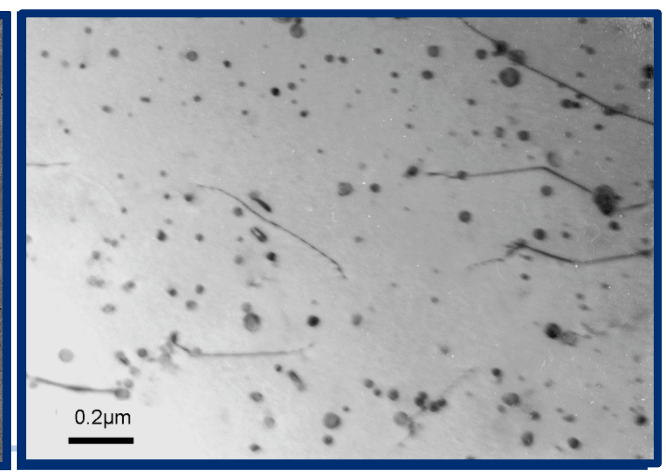




As-HIP 850°C



As-HIP 1300°C



As-HIP 1300°C

Alloy Development

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CR-118Ti Microstructure *(0.2 Y and 1.2 O at.%)*

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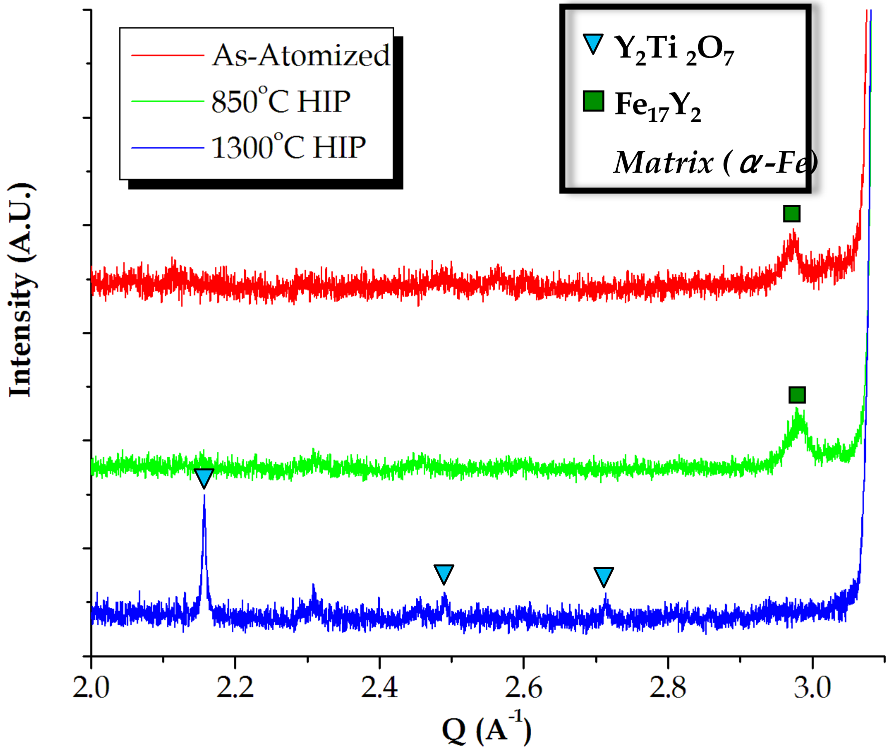

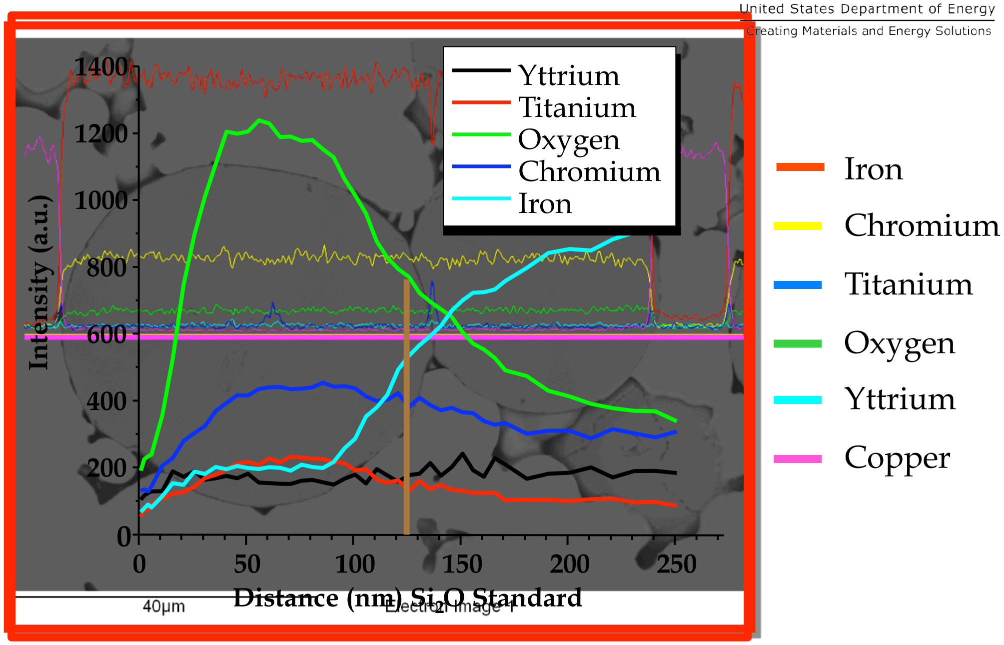

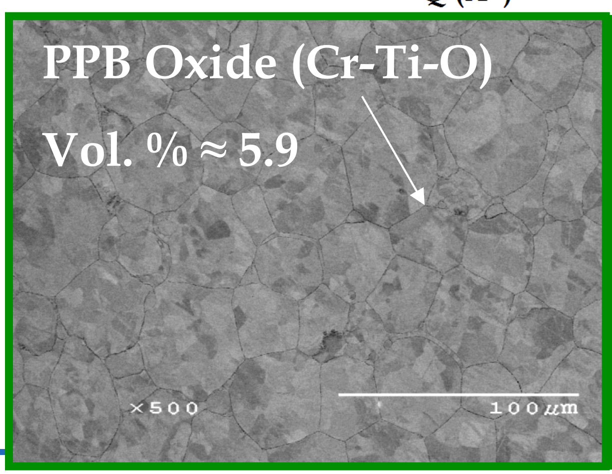

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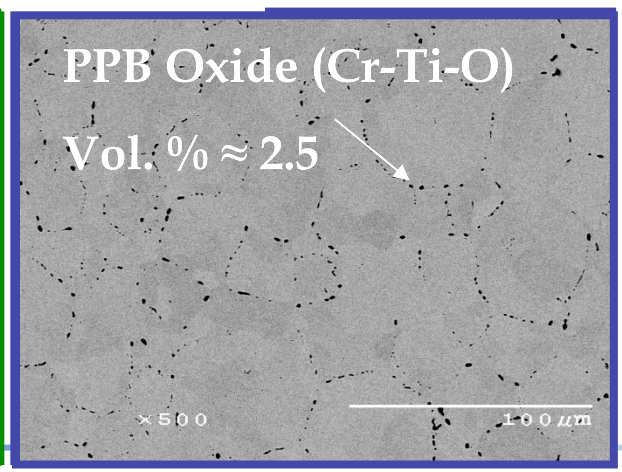

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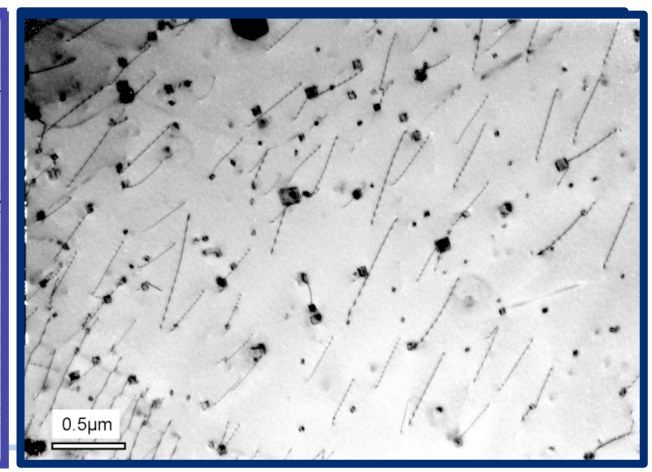

As-HIP 1300°C

Alloy Development

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Results

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CR-126TiW Microstructure *(0.1 Y and 0.5 O at.%)*

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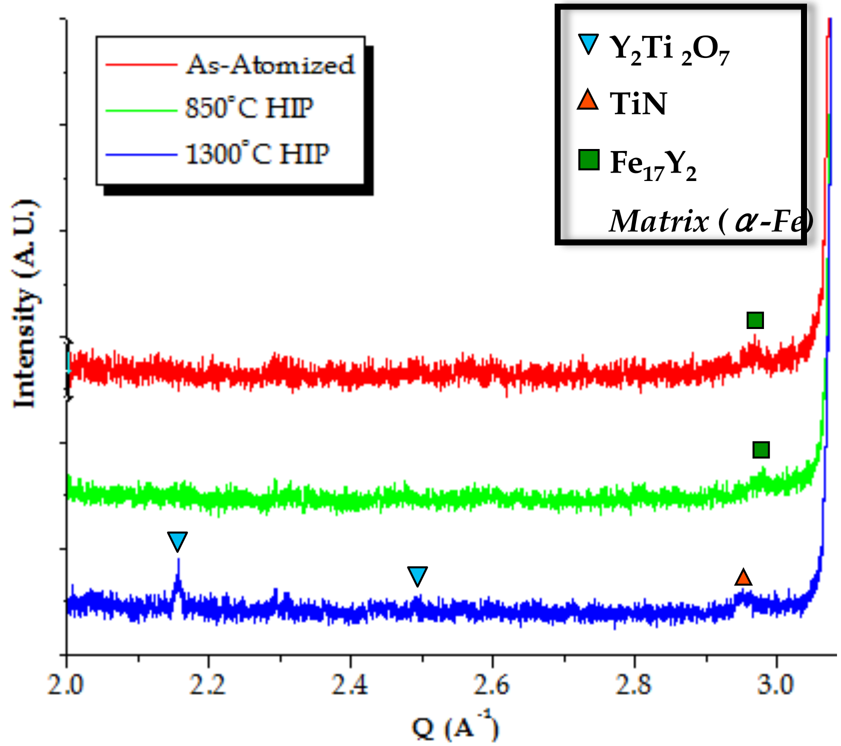

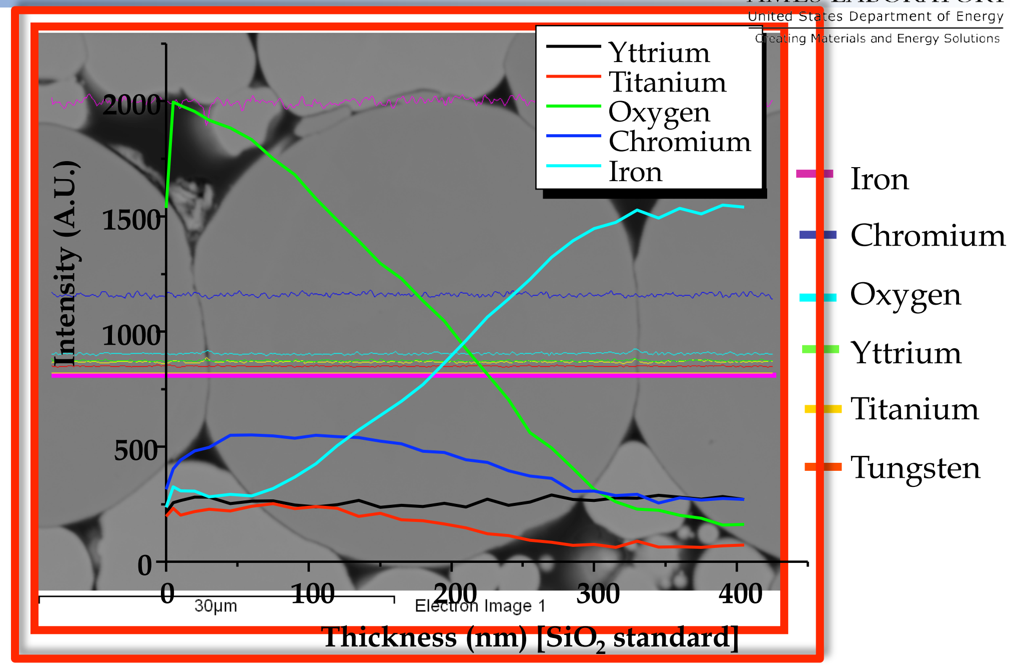

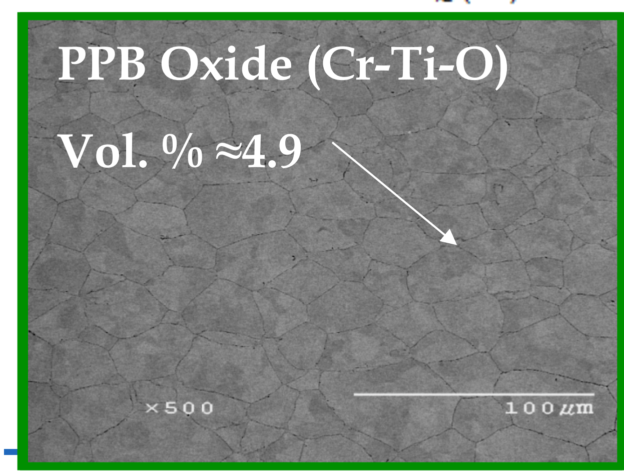

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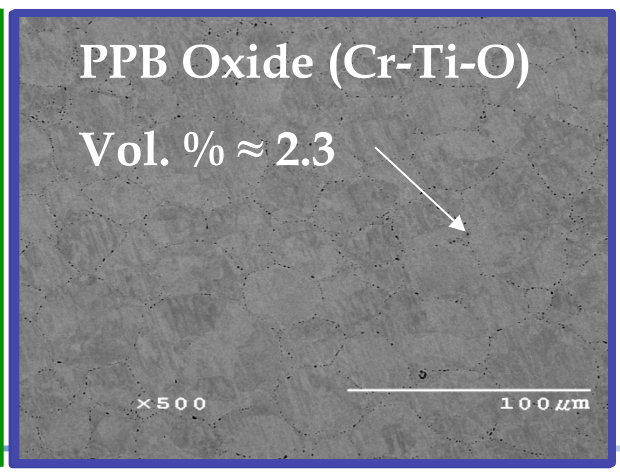

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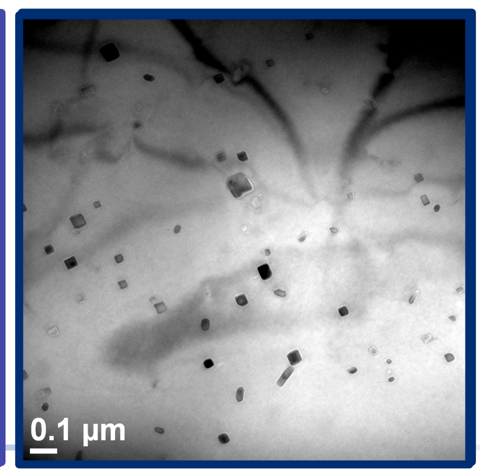

As-HIP 1300°C

Dispersoid Composition Importance

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- Dispersoid composition is dependent on alloying constituents
- The ideal ratio of yttrium-to-oxygen can vary with resulting dispersoid phase composition
- In all cases the dispersoids form as mixed oxides

Initial Alloy Design Y/0 ≈ 0.667 at.%

Y_2O_3	Atomic %	Weight %
Yttrium	0.400	0.500
Oxygen	0.600	0.135

Fe-Cr-Y Y/0 ≈ 0.33 at.%

$(Y,Cr)_2O_3$	Atomic %	Weight %
Yttrium	0.200	0.500
Oxygen	0.600	0.270

Fe-Cr-Y-Ti (wt.%) Y/0 ≈ 0.285 at.%

$Y_2Ti_2O_7$	Atomic %	Weight %
Yttrium	0.181	0.500
Oxygen	0.636	0.320

As-Consolidated Mechanical Testing

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Tensile Bar Specimen:

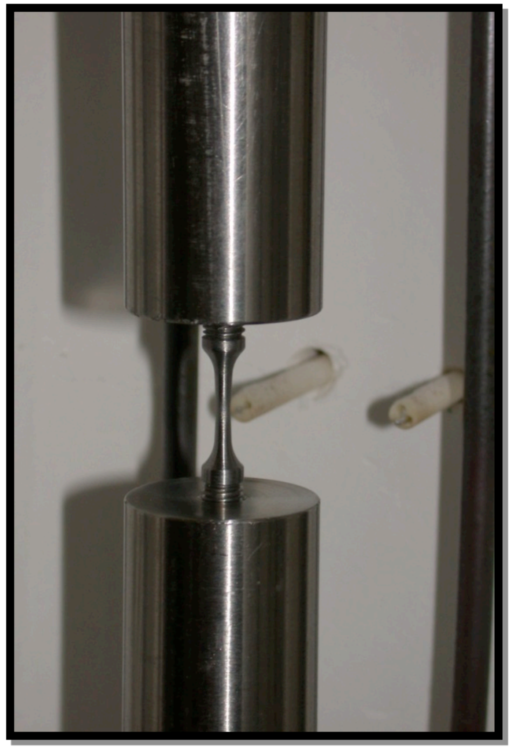
- As-HIP 1300°C – 4.0 hrs. – 303 MPa
- Finite Element Analysis Design

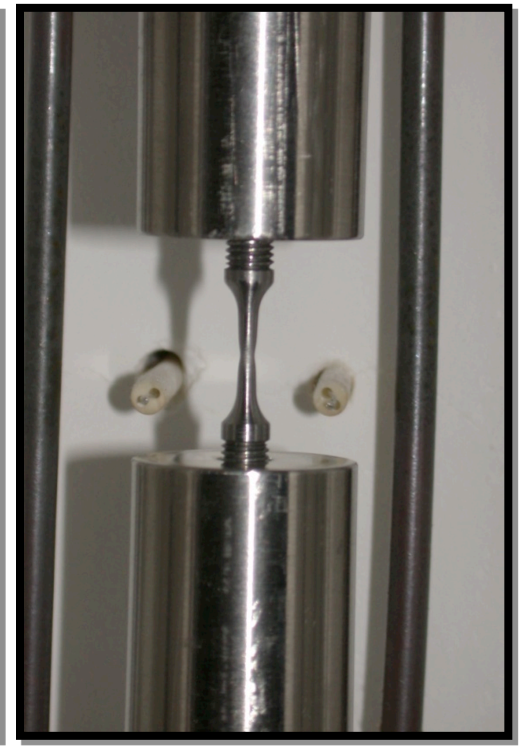
Open Air Tensile Test Machine:

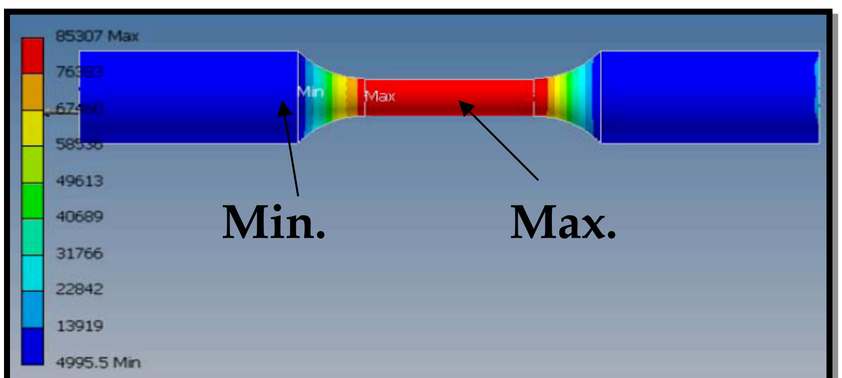
- 810 MTS-657.01 HT Furnace
- Temperature Range RT-800°C

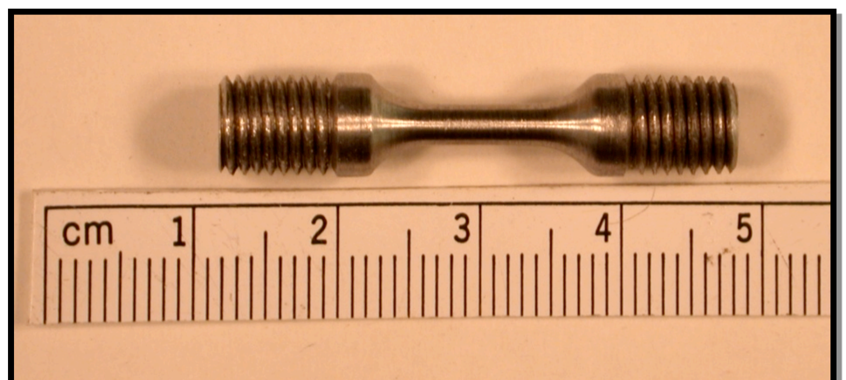
Test Procedure:

- ASTM-E 21-05 (HT Tensile Testing)
- Displacement velocity = 0.1 mm/min.









Tensile Strength Comparison

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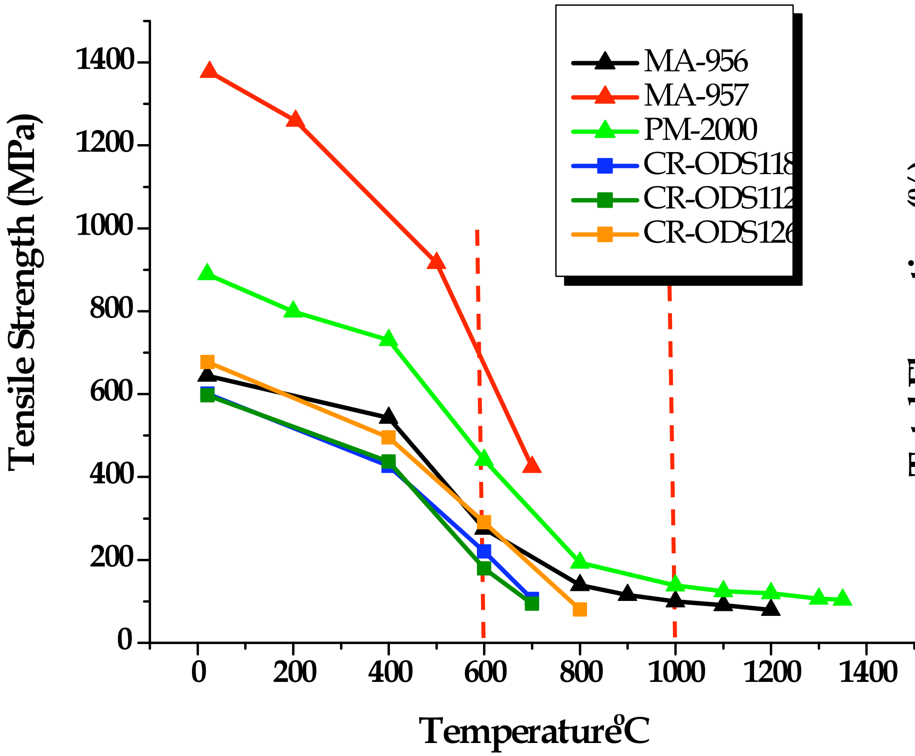
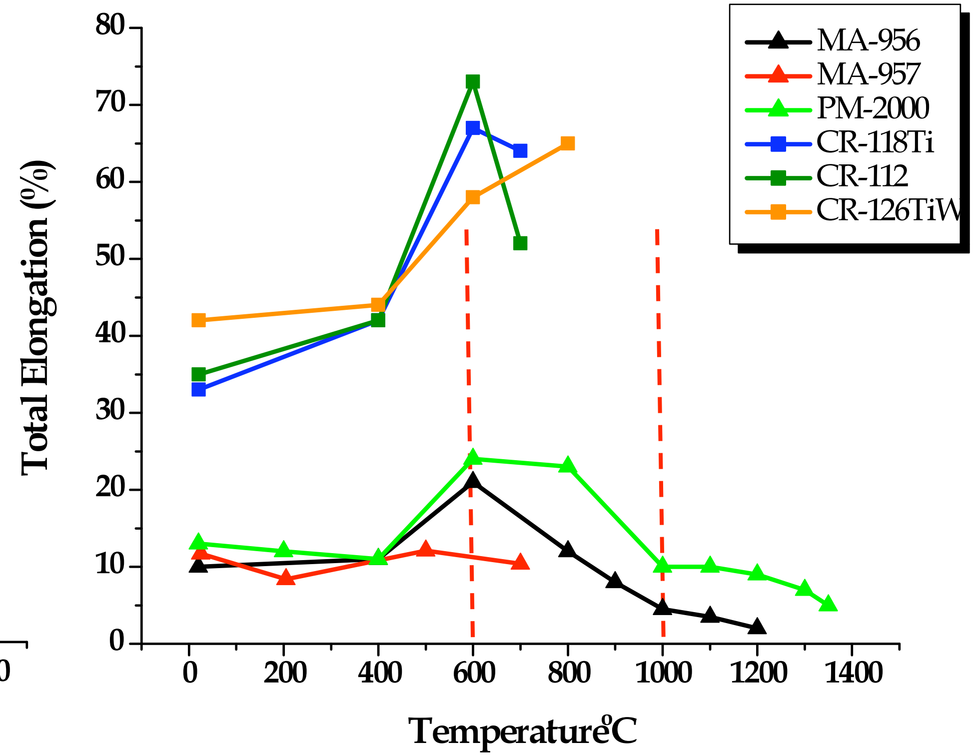
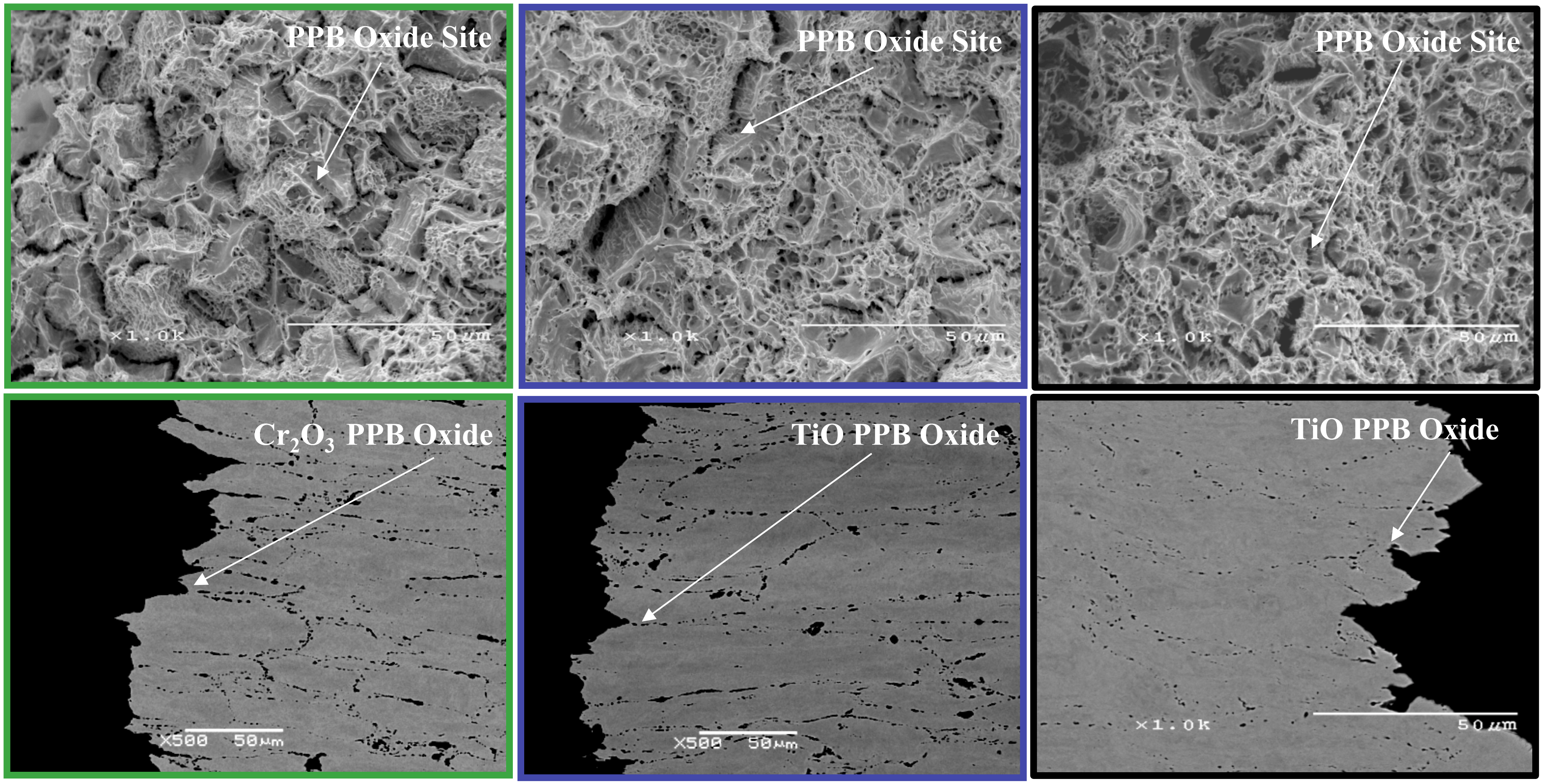




- **Similar tensile strength as MA-956 with about three times the total elongation**
- **All commercial alloys converge above 800°C**
- **CR-alloys were tested with a non-ideal microstructure (residual PPB oxide)**
- **All CR-Alloys illustrate similar tensile strength due to related isotropic microstructures and sub-optimal strengthening (no hot working)**

*R.L. Klueh et al., Oak Ridge National Laboratory, Journal of Nuclear Materials 341 (2005) 103-114

Failure Analysis-Microstructure



CR-112 **CR-118Ti** **CR-126TiW**

Failure occurs by micro-void formation/coalescence resulting from the debonding of the matrix from residual non-ideal phases (i.e. PPB oxide)

Summary

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Microstructure evolution

- A new simplified processing technique involving gas atomization and in situ oxidation has been developed to produce precursor ferritic stainless steel powder that can be consolidated into an oxide dispersion strengthened alloy with an isotropic microstructure.
- Results have shown a clear ability to manipulate the phase microstructure using high temperature consolidation.
- High energy synchrotron powder diffraction data and TEM microstructure analysis confirms the formation of oxide dispersoids during high temperature consolidation.

Mechanical Properties

- Alloy tensile strength seems limited to the interfacial bond strength between the residual PPB oxide and the α-Fe matrix.
- Global microstructure needs improvement (i.e. full dissociation of PPB oxide) to eliminate premature interfacial debonding.
- Atomization parameters and alloy design will need to be adjusted in order to achieve an optimum balance between initial oxygen content at the PPB's and (dissolved) yttrium concentration within the matrix to achieve fully transformed microstructure.
- With fully transformed microstructure, heat treating temperature and thermal mechanical processing will be investigated to enhance Orowan strengthening from dispersiods.

Future Work: Alternative Alloy Design

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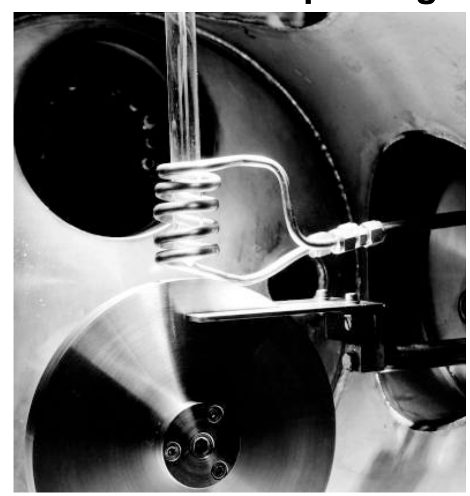
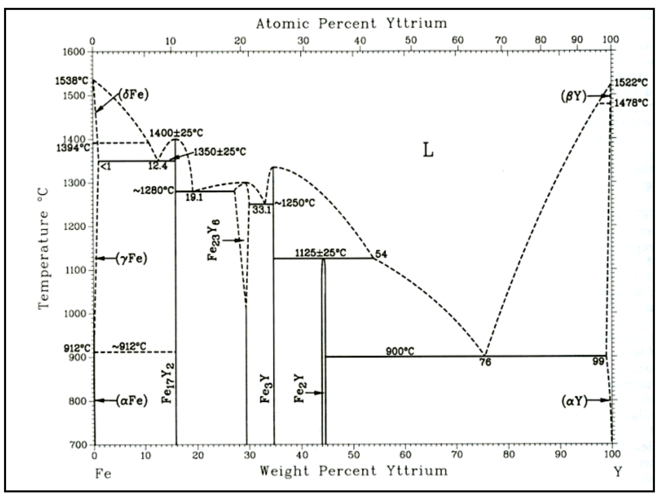
Rare earth (Y & Er) solute trapping limitations in Fe-based rapidly solidified powders:

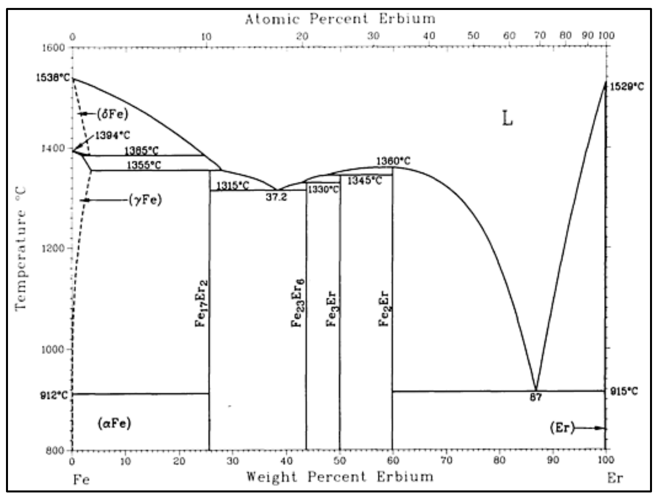
Fe-15Cr-(0.15-0.65)Y (wt.%)
Fe-15Cr-(0.15-0.65)Er (wt. %)

- Wheel speed: 30 m/s
- Similar solidification rates as He gas atomized powders with dia.< 10µm.

Cu-block Melt Spinning







Future Work: Reactive Gas Concentration

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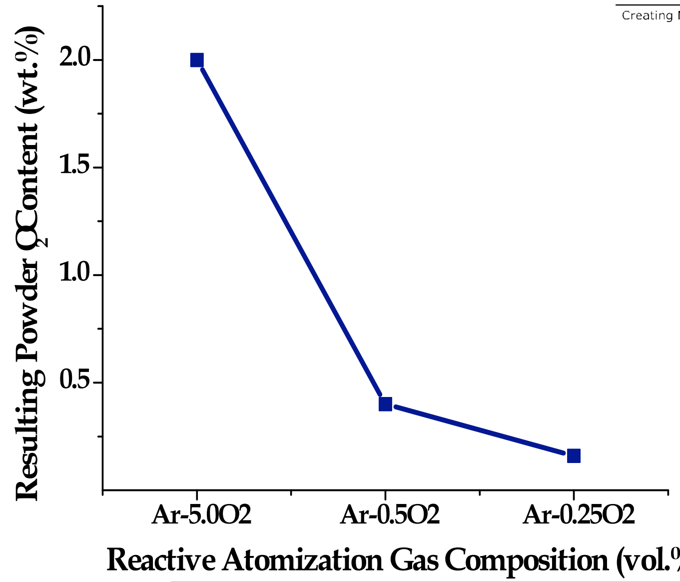
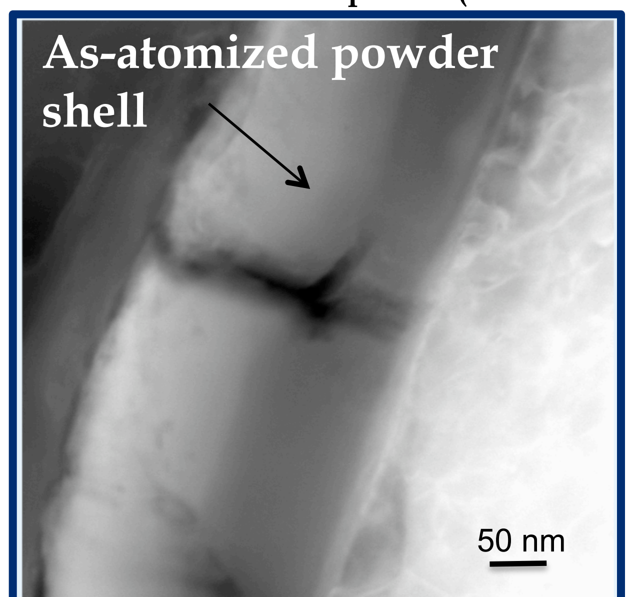
- Resulting oxygen concentration supplied by as-atomized powder particles is a direct function of reactive gas concentration.
- Oxygen concentration can vary with particle size (sieving control)
- High temperature rapid reaction kinetics are likely linear (interface controlled or diffusion controlled)
- Critical to achieve the proper balance between dispersoid forming element (e.g., Y) and oxygen concentration





By modifying the reactive gas composition the oxide layer thickness on the powder particles can be controlled

Future Work: Oxygen Diffusion Rate

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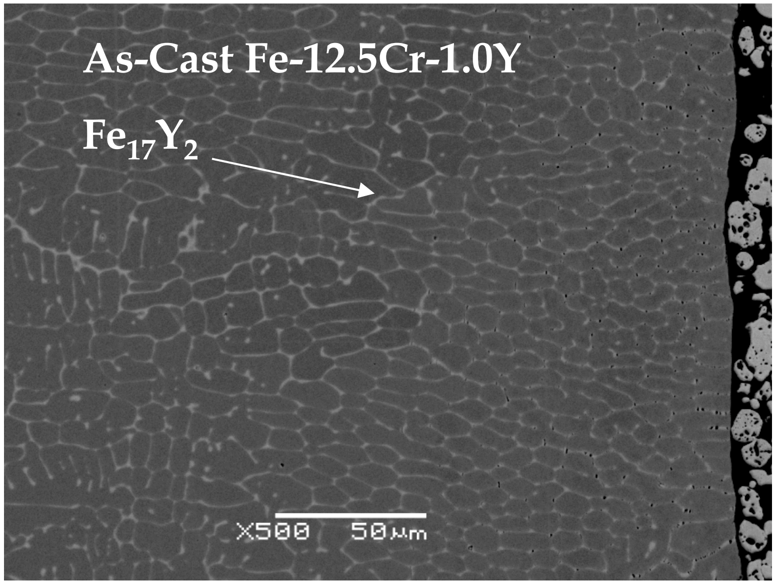
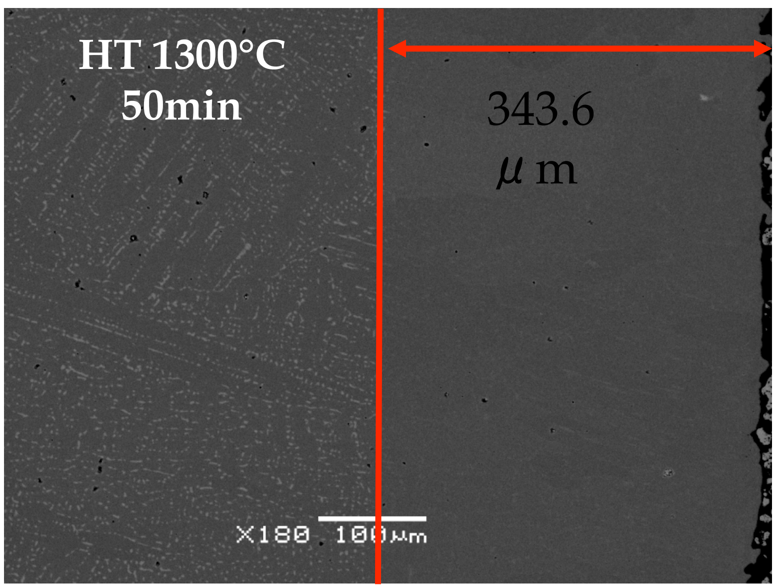
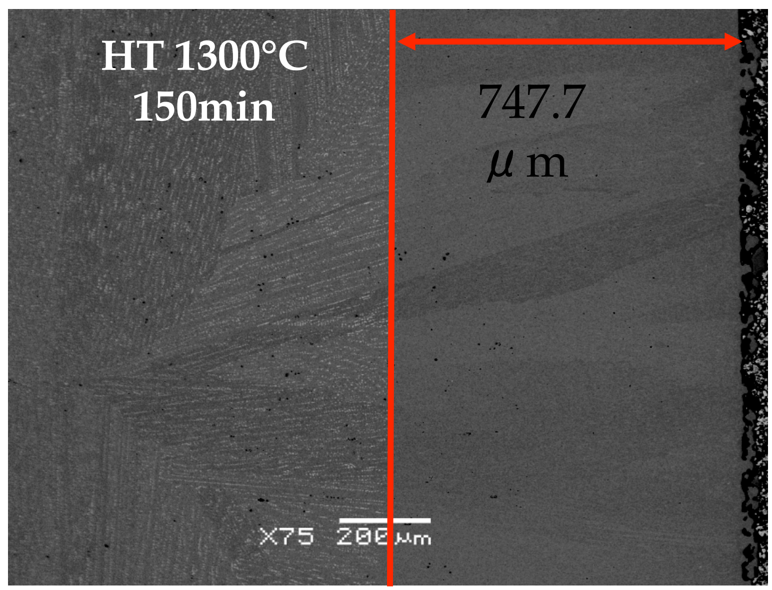


Rhines Pack (Cr_2O_3/Cr)

- Cr_2O_3 reducing conditions
- Oxygen dissociates $Fe_{17}Y_2$ ppts.
- Internal oxidation and precipitation of $(Y,Cr)_2O_3$
- Determine diffusion mechanism (boundary or bulk) by kinetics





Future Work: ODS Formation Reaction Rate

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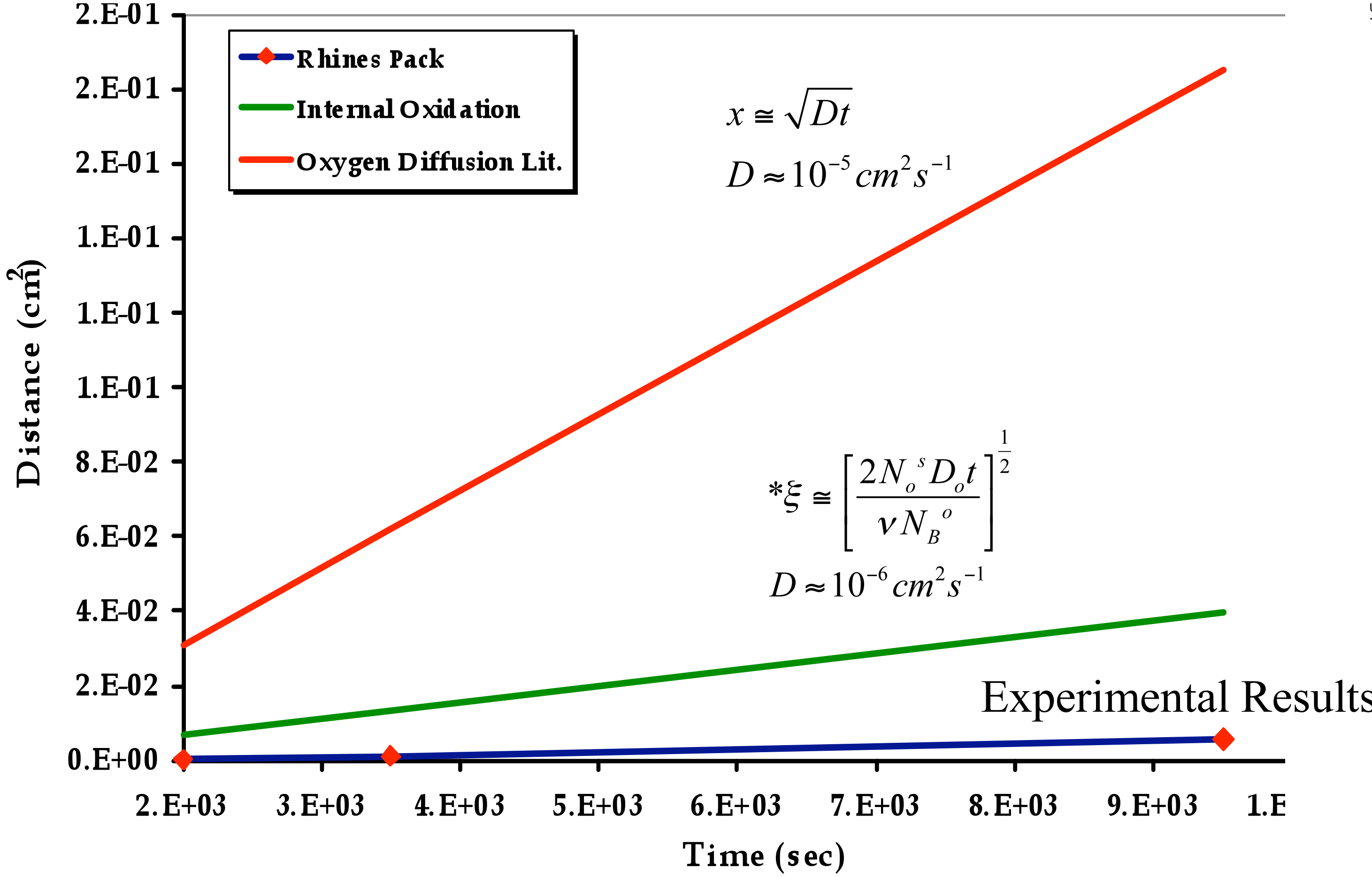

- Oxygen diffusion is very rapid at 1300˚C
- A diffusion distance of 25-30 μm requires only about 10 seconds
- Diffusion is not the rate limiting step in this reaction, i.e., could use lower temp.

*R.A. Rapp, Mechanism of Internal Oxidation, Corrosion-National Association of Corrosion Engineers, Vol. 21, 1965, 382-399.

**J.H. Swisher and E.T. Turkdogan, Trans. Met Sec. AIME, 1967, 239, 426.

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