Alloy Development

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ATI Allegheny Ludlum
An Allegheny Technologies Company

SECA Core Technology Program
SOFC Interconnection Technology Workshop
Argonne National Laboratory
July 28, 2004

Allegheny Technologies

Introduction

- Iron and nickel-base alloy design and development is a relatively mature science
- Helpful tools exist to aid in alloy development
- Transition from laboratory to practice is critical, complex, and often challenging

Overview

- Introduction to ATI Allegheny Ludlum and Allegheny Technologies
- Alloy design methodology and tools
- Alloy design for oxidation resistance
- Obstacles in transition from laboratory to practice
- Examples of ALC alloy development

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Materials	Stainless steel, Ni-base alloys, Ti (CP and alloy), Co-base alloys, Zr, Hf, WC, +++			
Product Forms	Sheet, Strip, Plate, Billet, Bar, Rod, Castings, Forgings, and Cutting Tools			
Sales Distribution	US 77% Europe 12%			
Primary Markets (2003 annual report)	Aerospace Automotive Power Gen	18% 12% 11%	CPI / O&G Appliance Cutting Tools	10% 10% 10%
ATI Operating Companies	Allegheny Ludlum, Allvac, Wah Chang, Metalworking Products, Portland Forge, Casting Service			
ATI Joint Ventures	STAL, UNITI			

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ATI Allegheny Ludlum Products

Stainless Steels and Specialty Alloys

Austenitic (Fe-Cr-Ni)	Ferritic (Fe-Cr)
Type 201L Types 301, 304, 316, 317, 321, 347 Types 309S, 310S AL904L™, AL-6XN®, AL4565™ alloys	Types 409, 409ALMZ™, 439, 444 AL453™, E-BRITE®, AL 29-4C® alloys ALFA™ I, II alloys (FeCrAl)
Duplex (Fe-Cr-Ni)	**Precipitation-Hardening (Fe-Cr-Ni)**
AL2003™, AL2205™, AL255™ alloys	AL286™ alloy AL13-8™, AL15-5™, AL15-7™, AL17-4™, AL17-7™ alloys AM350™, AM355™ alloys
Specialty	**Titanium**
Grain oriented silicon steels Controlled magnetic property alloys Controlled CTE (AL36™, AL42™ alloys) Armor plate (K12® Armor Plate) Tool Steels	CP grades 1-4 Grades 5 (6-4) and 23 (6-4 ELI) Grades 7, 11, 16, 18 (Pd-bearing)

Nickel-Base Alloys

Heat-Resistant Grades	Corrosion-Resistant Grades
AL800™/AL800H™, AL825™, AL600™, AL601™ alloys ALTEMP® 625, ALTEMP® 718, ALTEMP® HX, ALTEMP® 263 alloys, X-750 alloy	AL22™, AL276™, ALLCOR®, AL400™ alloys

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ATI Allegheny Ludlum Technical Center

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Technical Center

Functions

- Stainless Steel, Nickel and Titanium Alloy Development
- Product Improvement
- Process Improvement
- Failure Analysis
- Welding Process Development
- Corrosion Testing
- Oxidation Testing
- Mechanical Testing (non-production)

Facilities

- Melt Shop (50 lb VIM)
- Process Lab
  (4 Rolling Mills, Forge Press, Furnaces)
- Metallography Lab
  (Sample Preparation, Microscopes)
- Scanning Electron Microscope
- Scanning Auger Microprobe
- Corrosion Lab
- Oxidation Lab
- Mechanical Behavior Lab
- Welding Lab
- Annealing Simulation (Gleeble) Lab

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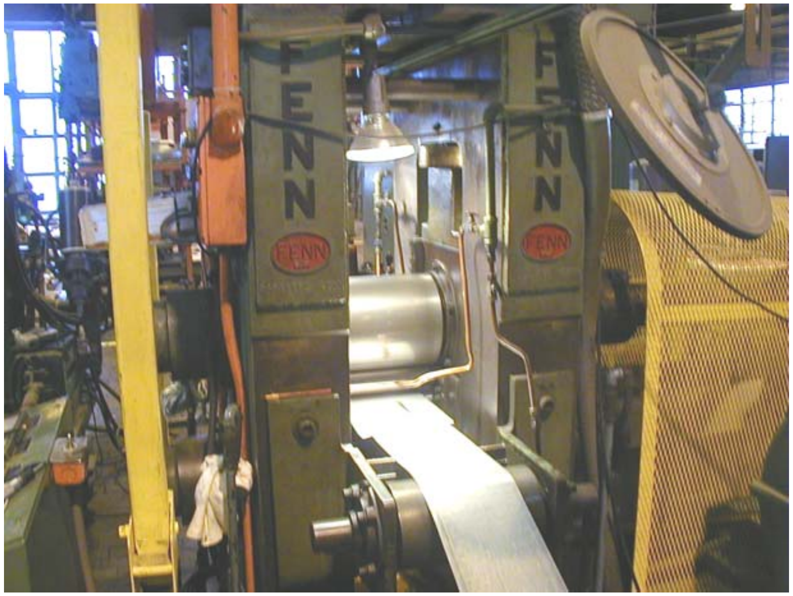

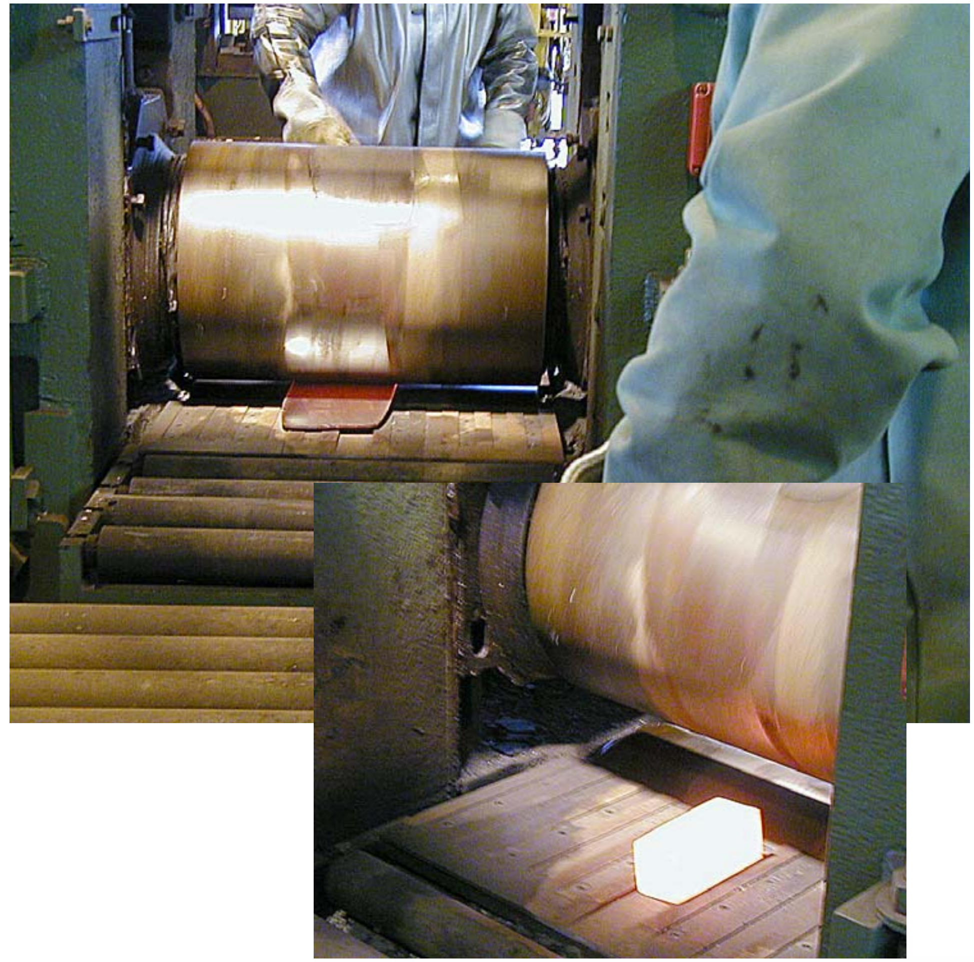

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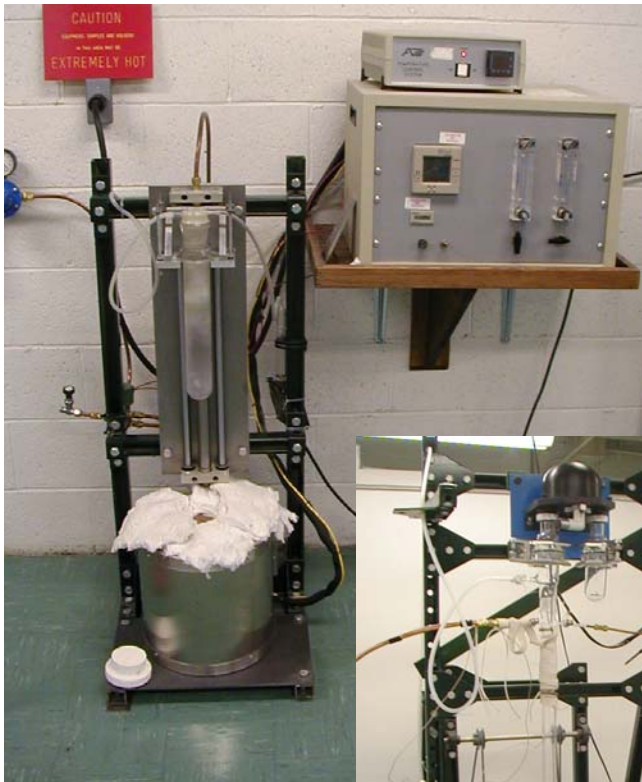

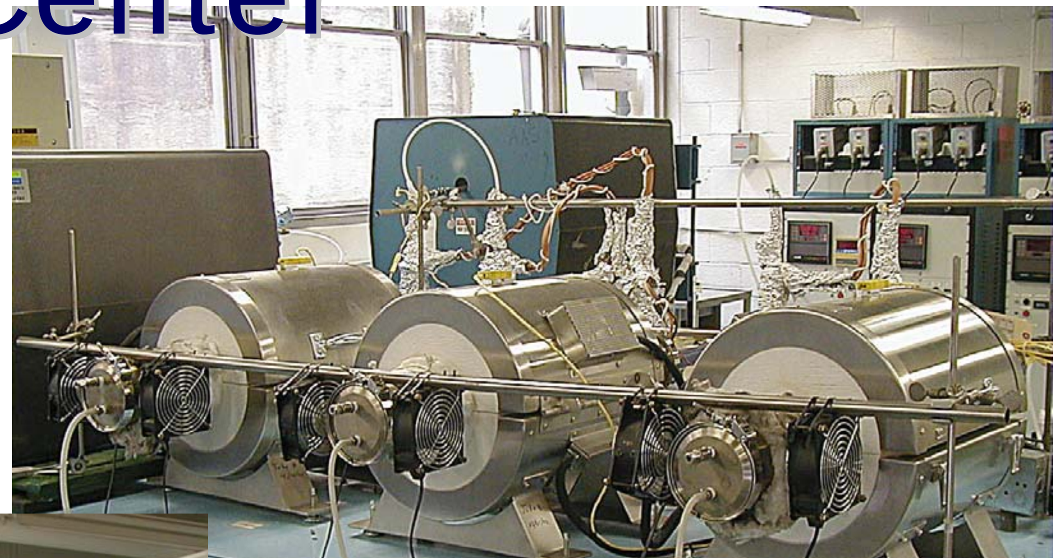

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Alloy Design and Development

- Development of new/unique alloys is not as common as in the past
- Most projects involve modifying existing alloys for a specific need or market
  - Performance improvement
  - Cost reduction
  - Process enhancement
- Well-established methods and tools exist to aid in alloy design

Design for Oxidation Resistance

- Traditional methods for designing heat-resistant alloys involve the concept of selective, protective oxidation
  - Useful protective oxides are Cr_2O_3, Al_2O_3, SiO_2
  - Choice depends on application
    - Temperature
    - Environment
    - Strength requirements
    - Required operating lifetime
    - Cost
  - Incorporate sufficient amount to form and maintain an external oxide scale
  - Most wrought heat-resistant alloys rely on chromium oxide

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Design for Oxidation Resistance

- Secondary alloying effects can be utilized to increase oxidation resistance
  - Add an element which exhibits intermediate oxide stability (e.g. FeCrAl alloys)
  - Add rare earth elements to increase adhesion, reduce growth rate
  - Some oxides can be doped, which alters the defect structure and growth rate

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Design for Oxidation Resistance

- Mitigate unwanted alloying effects
  - Phase stability issues
    - TCP phases
    - Laves
    - Ferrite-austenite balance (stainless steels)
  - Rapid precipitation of strengthening phases
    - Hot working
    - Coiling
  - Rare earth over-doping
    - Excessive oxidation
    - Workability problems

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Design for Oxidation Resistance

- Protective oxides typified by…
  - Compact
  - Adherent
  - Slow-growing
  - Low concentration of charged electronic / ionic defects
- SECA goals may require non-traditional design concepts
  - Protective oxides generally poor electrical conductors
  - Chromium oxide proven to be volatile in the presence of water vapor to levels damaging to SOFC components

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Design for Oxidation Resistance

- Extensive theoretical work exists to predict oxidation behavior of alloy systems and to aid in the interpretation of experimental data
  - Theory of diffusion-controlled oxidation (Wagner)
  - Theory of transition from internal to external oxidation (Wagner)
  - Rate law theory (many)
  - Various thermodynamic diagrams

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Empirical Design

- Identify required properties
  - Mechanical properties
  - Physical properties
  - Corrosion/oxidation resistance
  - Formability
  - Cost
- Correlate required properties with existing knowledge
  - Do you need a new alloy?
  - Where should you begin?

Design Tools

- Alloy selection tools
  - Handbooks
  - Software (e.g. CES4 - Granta Design)
- Phase diagrams
- Constitutive equations
- Computer modeling

Constitutive Equations

- Simple predictive expressions
- Developed by analysis of large data sets
- Single purpose
- Generally of limited applicability
- Good for predicting effects of minor variations in composition, processing, etc.

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Constitutive Expressions

Ferrite Number (δ ferrite)

$FN = 3.53(Cr_{eq}) - 2.61(Ni_{eq}) - 30.03$

$(Cr_{eq}) = [Cr]+[Mo]+1.5[Si]+2.27[Ti+V]+0.5[Nb+W]+0.21[Ta]$

$(Ni_{eq}) = [Ni]+30[C+N]+0.5[Mn]+0.4[Cu+Co]$

Electron Vacancy (TCP phases)

$N_V = 0.66[Ni] + 1.71[Co] + 2.66[Fe] + 4.66[Cr+Mo+W] + 5.66[V] + 6.66[Zr] + 10.66[Nb]$

Sigma Solvus

$T_s = \{26.4[Cr] + 6.7[Mn] + 50.9[Mo] + 92.2[Si] + 447\} - \{9.2[Ni] + 17.9[Cu] + 230.4[C] + 238.4[N]\}$ *Rechsteiner*

Pitting Resistance Equivalency (relative corrosion resistance)

$PRE_N = [Cr]+3.3[Mo]+X[N] \qquad X = 16 \text{ or } 30$

Coefficient of thermal expansion (Ni-base alloys)

$\alpha_L = 13.87 + 0.073[Cr] - 0.080[W] - 0.082[Mo] - 0.018[Al] - 0.163[Ti]$ *Yamamoto et. al.*

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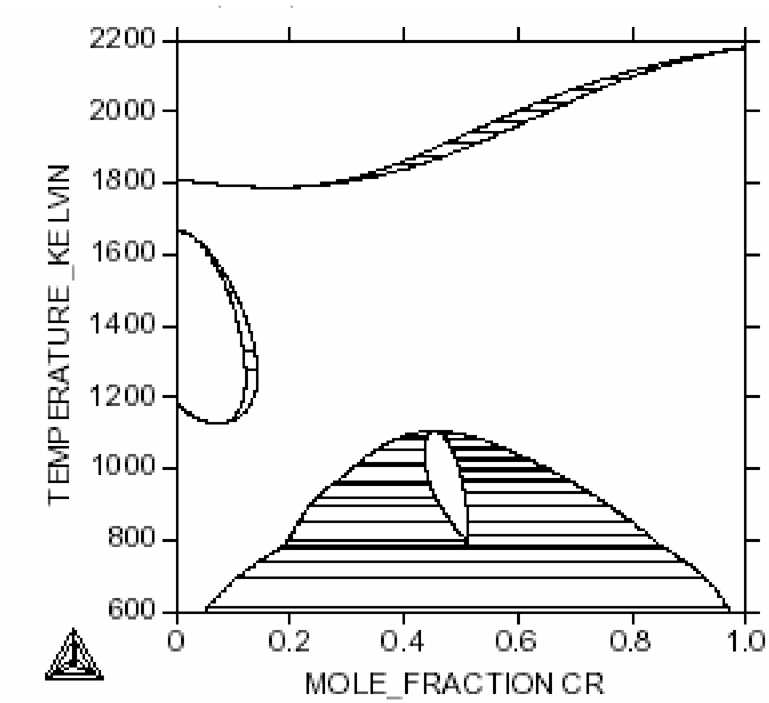
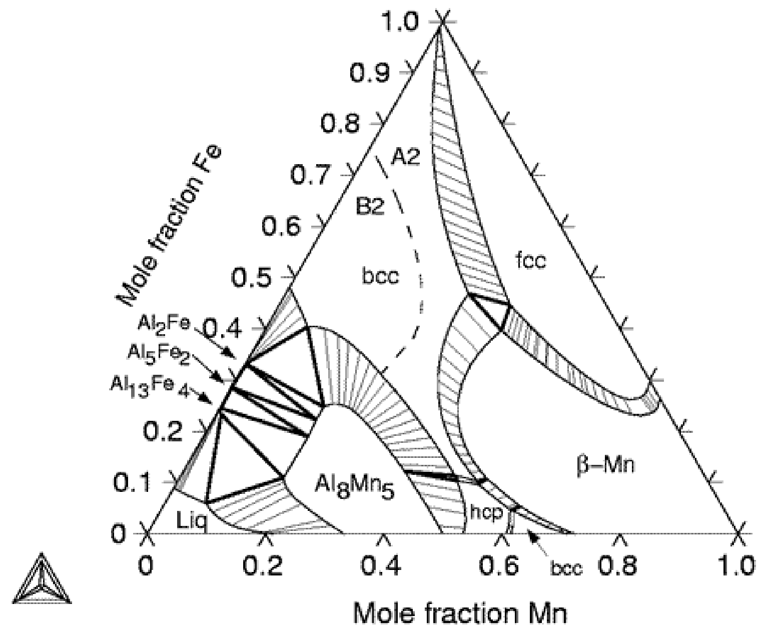
Computational Design

- Thermodynamic models (Thermo-Calc, JMatPro software)
  - Prediction of equilibrium phase balances via free energy minimization methods
  - Input factors include alloy composition, state variables
  - Generate phase diagrams, stepped output (temperature, composition)
  - Prediction of static situations

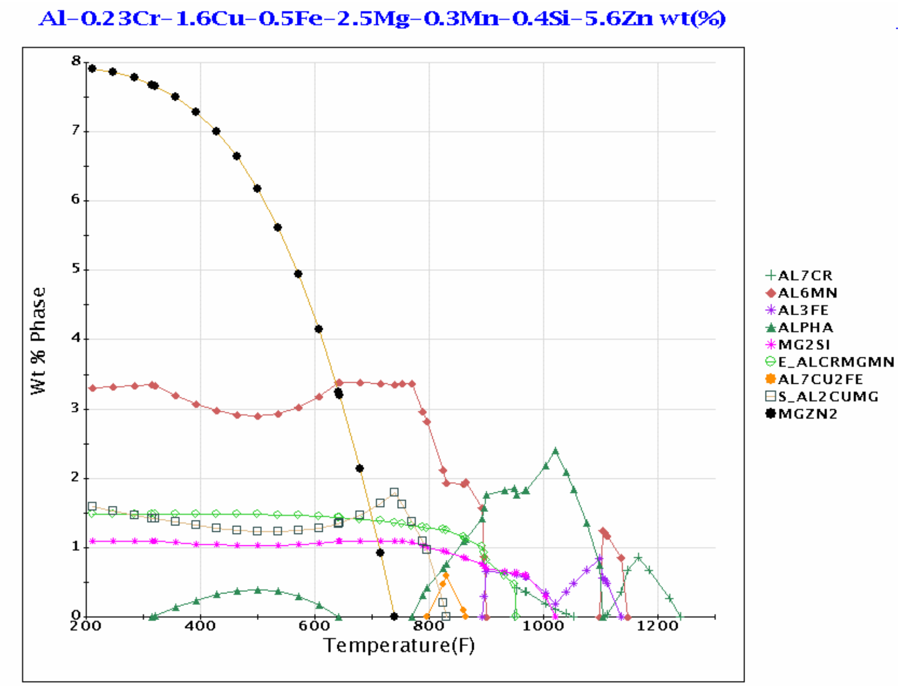
Computational Design

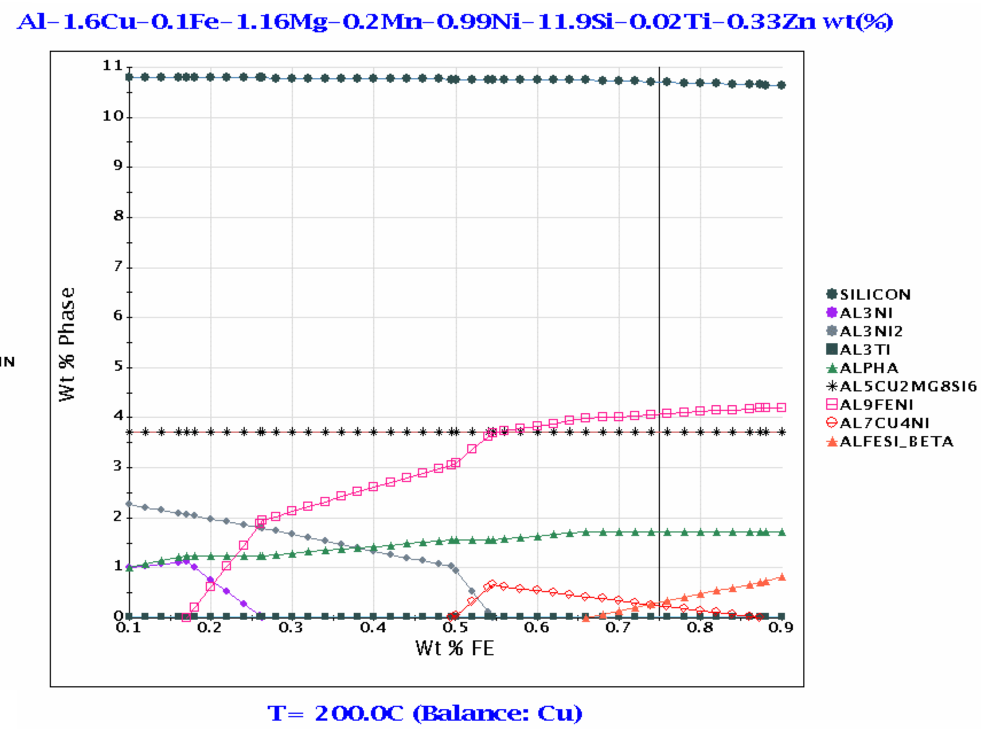




Diagrams from Thermo-Calc example manual

Computational Design





Diagrams from JMat-Pro example manual

Computational Design

- Recent software packages include a wider array of functions
  - JMatPro
    - Physical, mechanical properties
    - Lattice mismatch
    - TTT and CCT diagrams
    - Particle coarsening

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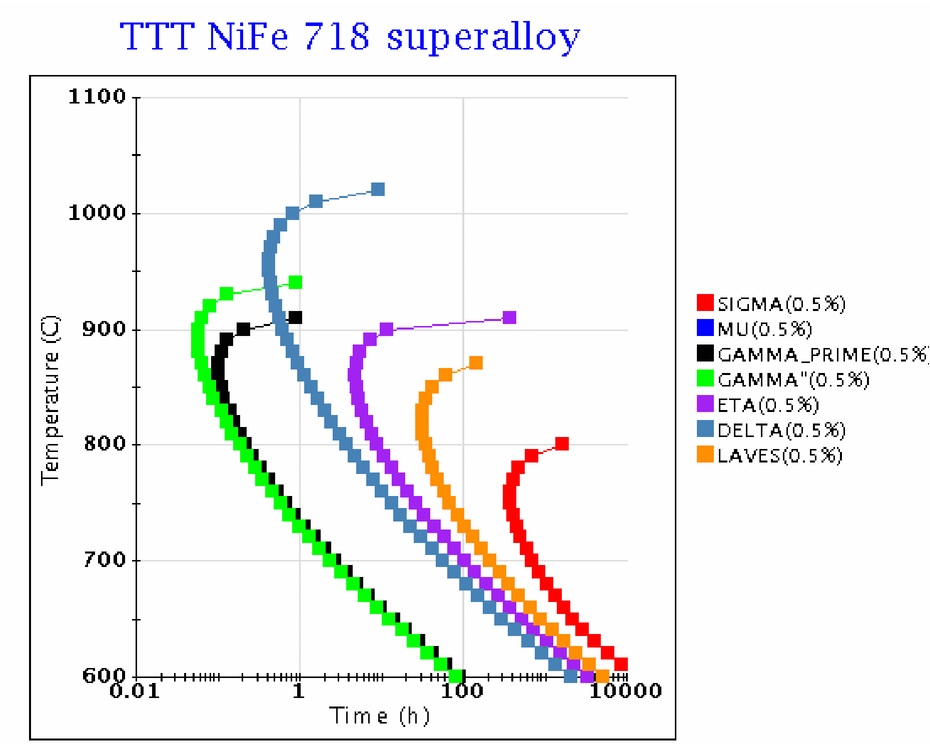
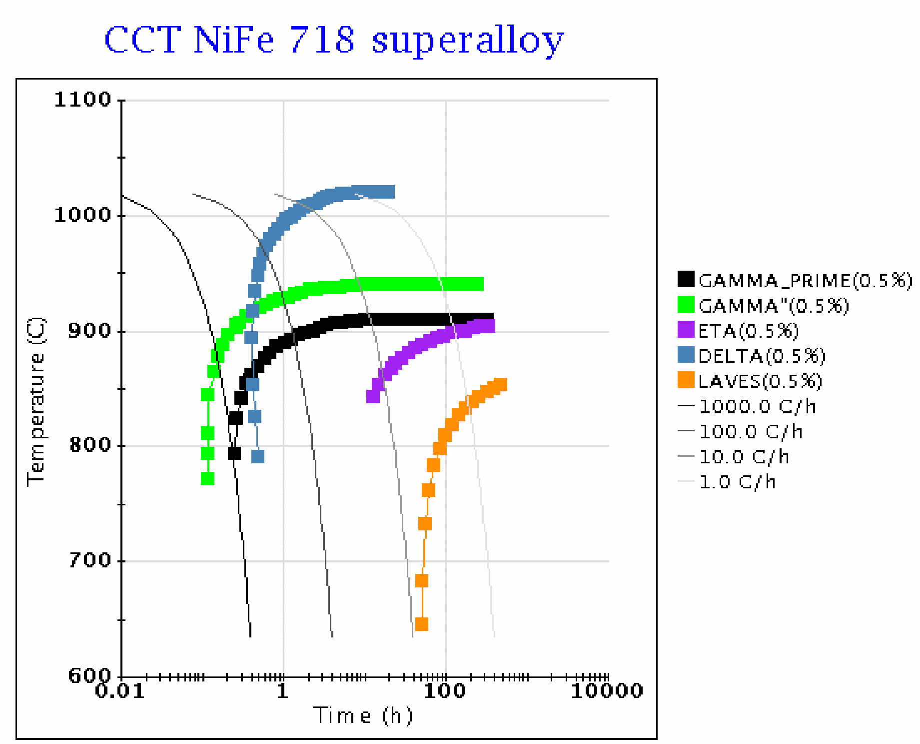
Computational Design





Diagrams from JMat-Pro example manual

Computational Design

IN939 nickel superalloy heat treated at 720C

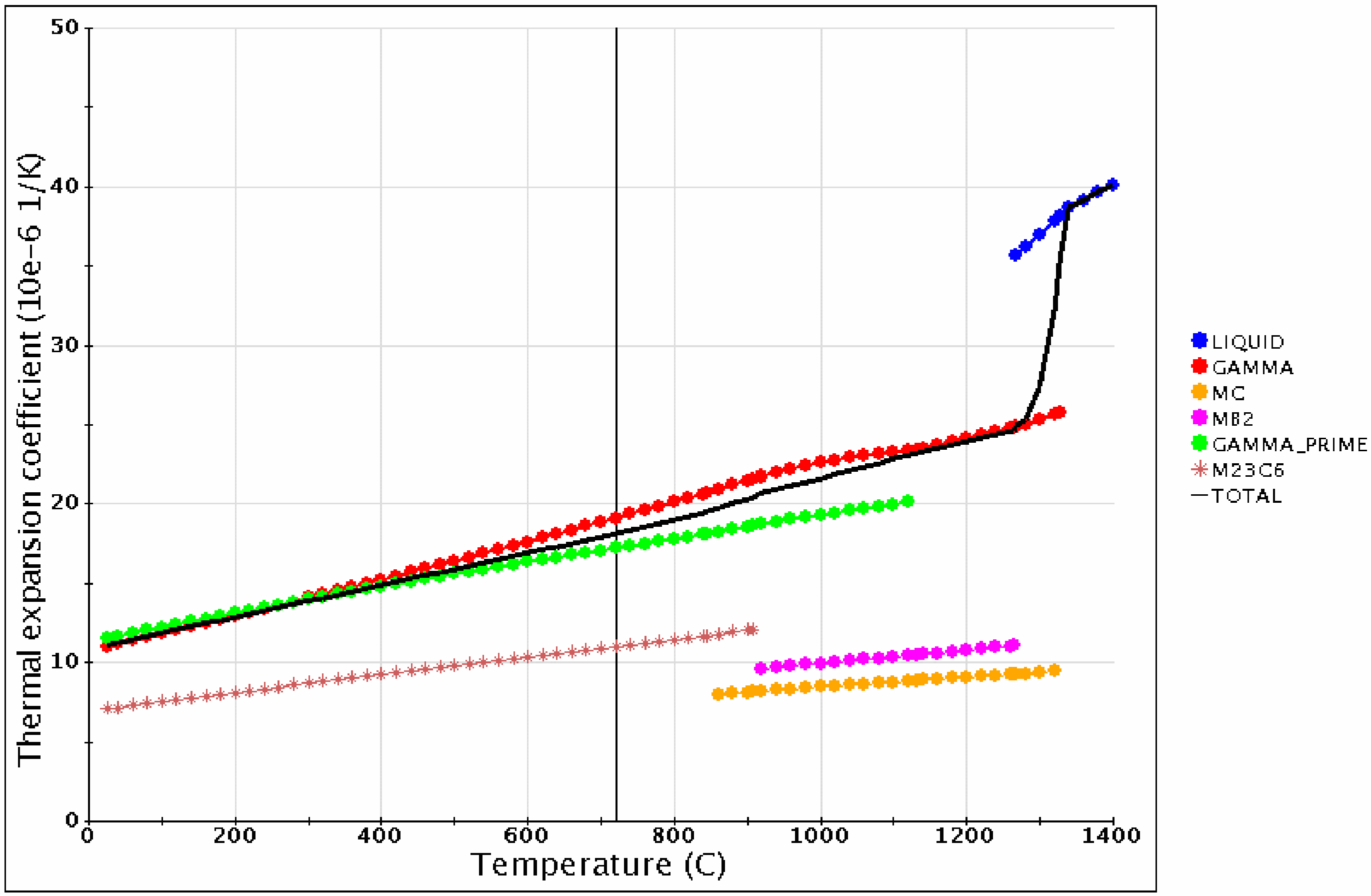


Diagram from JMat-Pro example manual

Computational Design

- Recent software packages include a wider array of functions
  - JMatPro
    - Physical, mechanical properties
    - Lattice mismatch
    - TTT and CCT diagrams
    - Particle coarsening
  - DICTRA
    - Diffusion in multi-component systems

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Computational Design

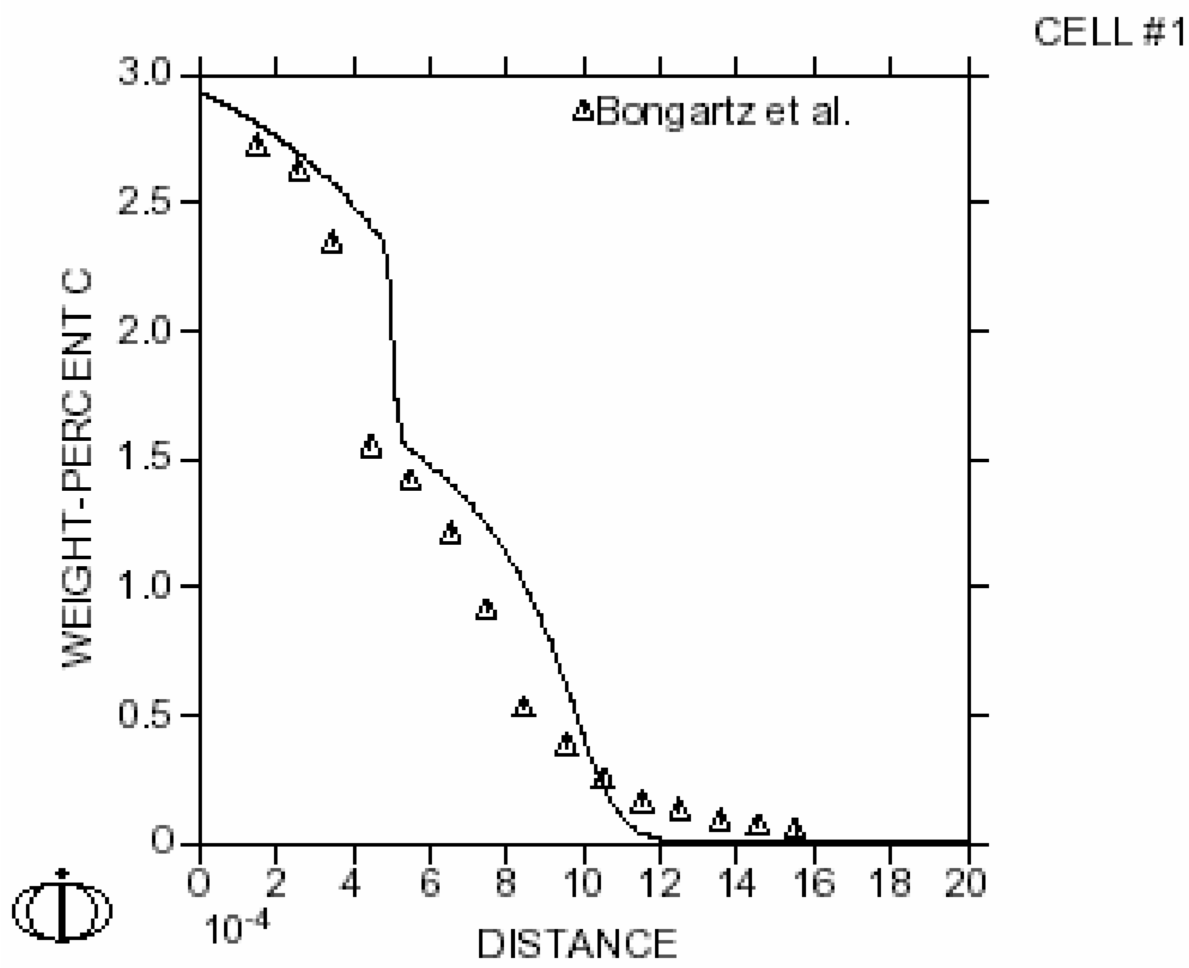

Diagram from DICTRA example manual

Computational Design

- Strengths
  - Rapid analysis
  - Inexpensive to run numerous trials
- Shortcomings
  - Only as good as the systematic assessment
  - Assumes equilibrium conditions
  - Requires experimental analysis and verification
  - Can be difficult to use

Computational Design Tools for Oxidation Resistance

- Few computational tools exist for predicting phase formation
  - A combination of thermodynamic and diffusion models should be able to address problem
- Some recent tools based on observations have become available to predict oxidation behavior under certain conditions
  - COSP for cyclic oxidation and spallation (Smialek-NASA)
  - ASSET alloy selection program (John-Shell/MTI)
- Custom approaches - ALC example
  - Lifetime map for metal foil
  - Oxidation and creep are active
  - Phenomenological model based on experimental data

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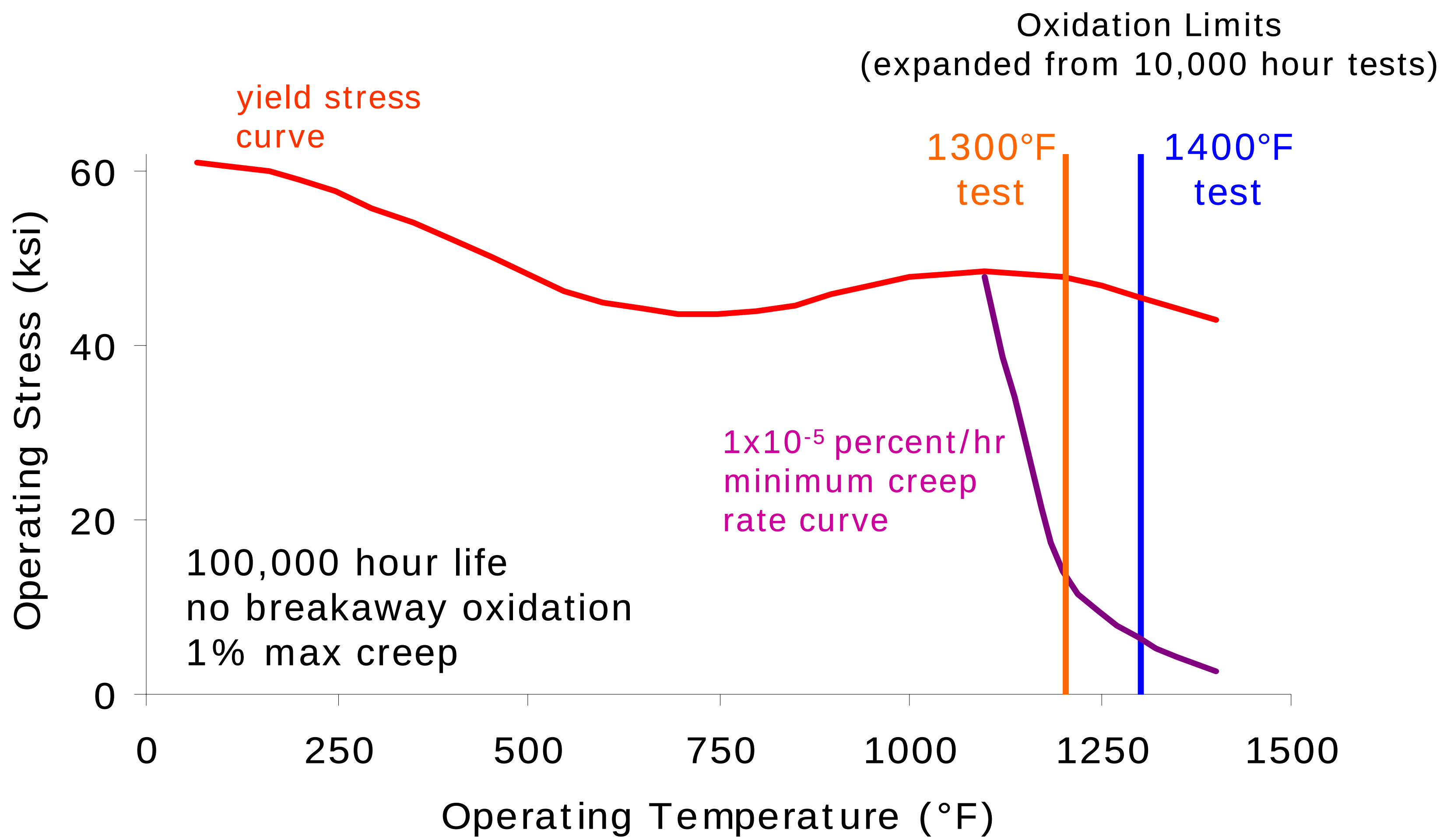
Lifetime Map for Metal Foil



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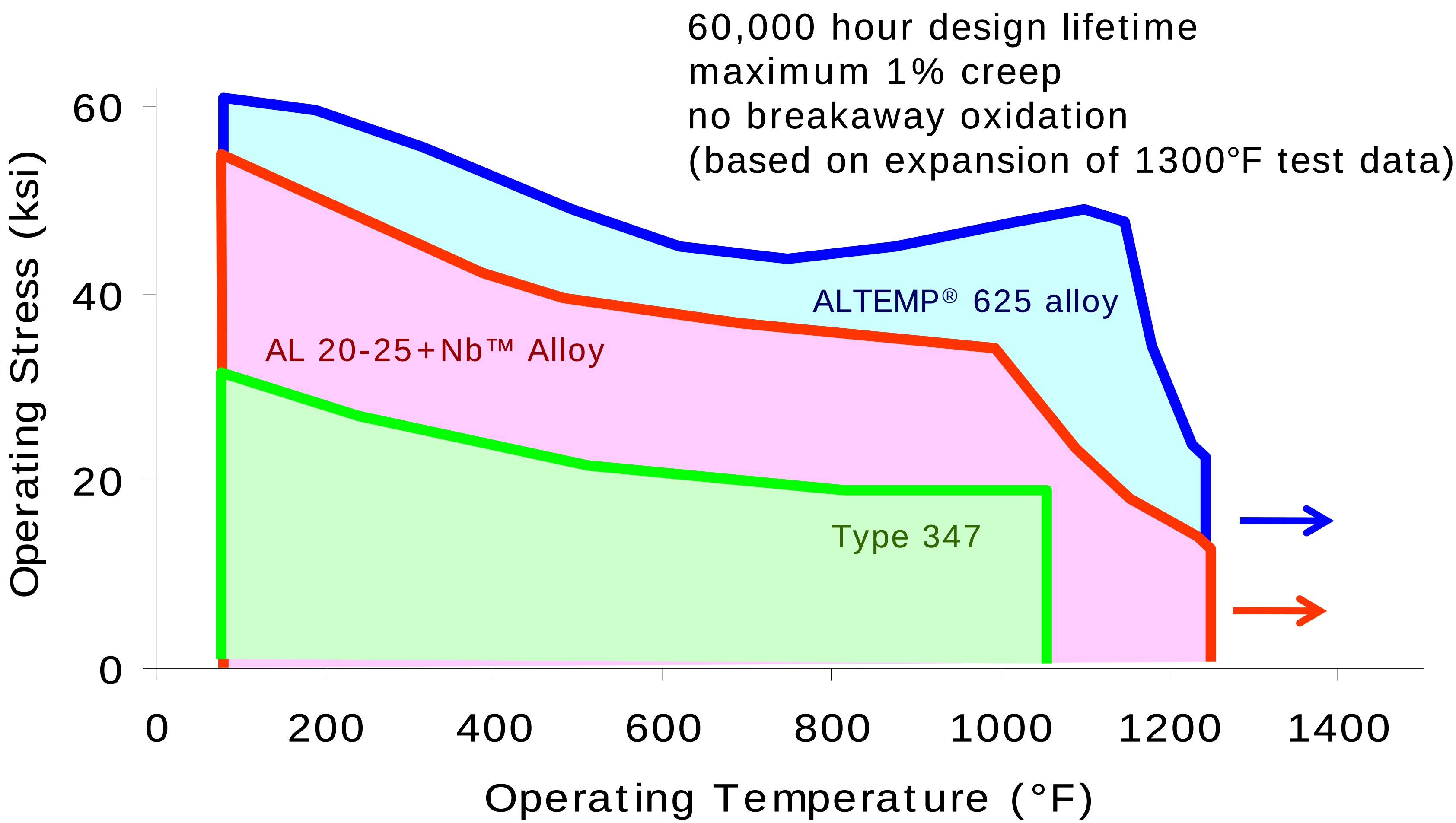
Lifetime Map for Metal Foil



Design of Experiments

- Utilize statistical methods and tools to construct experimental program
- Select critical variables
- Allow to vary in a controlled fashion
- Analyze the results to determine
  - Main effects of primary factors
  - Interactions between factors

Factorial Analysis

- Factors are critical variables
- Levels are quantitative or qualitative (e.g. high or low) factor values
- Provides more information than varying one factor at a time
  - Yields main effects of individual factors
  - Yields interactions between factors that simple approach overlooks
  - Proper use of randomization and repetition reduces sensitivity to baseline conditions

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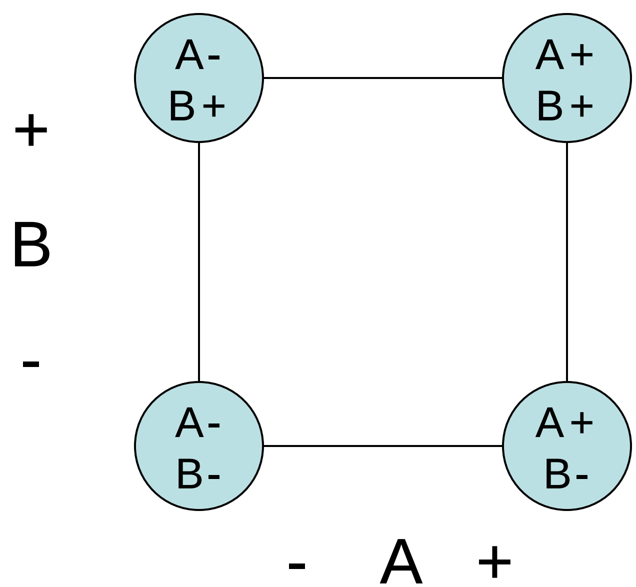
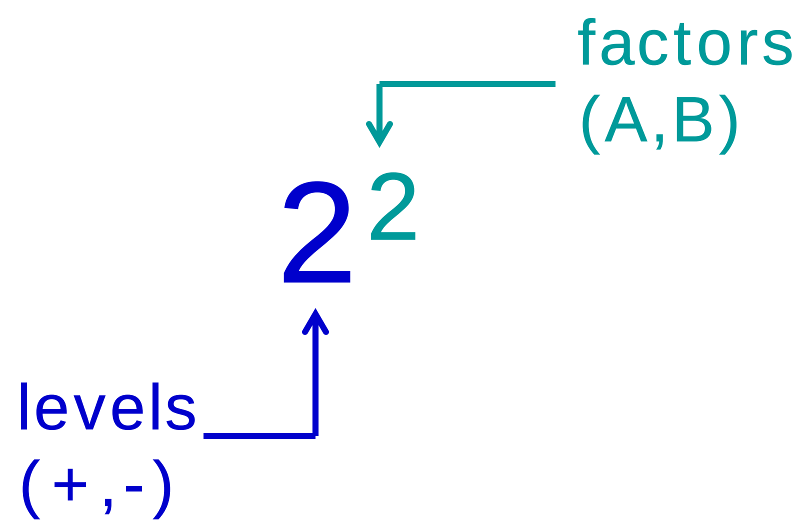
Factorial Analysis

- Simplest example is a two factor DOE experiment





four experiments

Factorial Analysis

- Simple or highly focused experiments can be run full-factorial
- Factorial analysis scales quickly to large numbers of experiments when numbers of factors is high

	number of experiments	
number of factors (k)	2 levels 2^k	3 levels 3^k
2	4	9
3	8	27
4	16	81
5	32	243
6	64	729
7	128	2.187
8	256	6,561

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Fractional Factorial Analysis

- Permits down-selection and significant reduction in required number of tests
- Yields less information, particularly for higher order interactions
- Higher order terms (3^{rd} order and above) are generally not significant
- If any factor is not statistically significant, fractional factorial collapses to a full factorial
- Some effects will be confounded and cannot be evaluated separately (aliased)
- Resolution must be selected carefully to produce useful information
- DOE tools used to generate test matrices and to determine aliased effects

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Transition to Production

- Transition from design to production can be difficult
- Limited by available production methods and economics
- What works on a laboratory-scale may not work in a production plant

much larger
much faster
far less forgiving

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Lab-Scale Alloy Production

- Melting
  - Small vacuum-melted buttons (< 1 pound)
  - Larger ingots (20-300 pounds) from VIM or VIM/ESR furnaces
- Product form
  - As-cast pieces
  - Small forgings
  - Narrow hand-rolled sheet and very small coils

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Mill-Scale Production

- Melting
  - Small heats
    - Vacuum-melted as small as 1,000 pounds
    - Air-melted as small as 10 tons (20,000 pounds)
  - Large heats
    - Vacuum-melted up to 15 tons (30,000 pounds)
    - Air-melted up to 180 tons (360,000 pounds)
- Product forms
  - Large coils, plates, bars, etc.
  - Quantities often restricted to product of a heat, particularly for sole-purpose alloys

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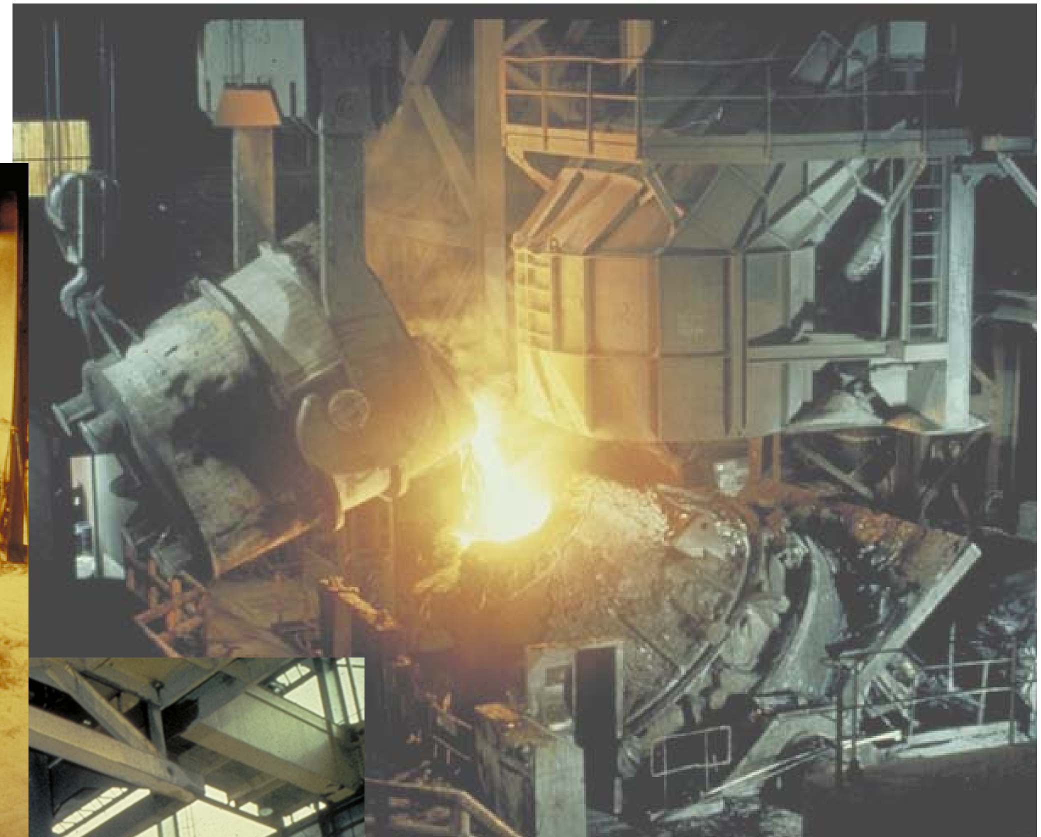
Melting



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Melting

- Low-cost air melting practices
  - EAF/AOD with continuous casting
  - EAF/AOD with ingot casting
  - EAF with continuous casting (limited)
- Higher-cost premium melting/remelting practices
  - VIM
  - ESR
  - VAR
  - Exotic practices (PM, PAM, EB, EB-CHR)

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Melting — Common Issues

- Elemental segregation
- Solidification cracking and defects
- Reactive element additions
- Volatile element additions
- Residual/minor element control

Melting Issues — Mitigation

- Minimize alloy additions which can be problematic
- Change to melting methods which minimize detrimental effects
  - Some alloys are difficult to continuously cast
  - Some alloys require special practices
  - Some alloys have to be remelted
    - Extreme tendency for segregation
    - Cleanliness requirements
- Some alloys cannot be produced by traditional melt methods

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Downstream Processing

- Hot rolling
  - Hot strip mill (once-through)
  - Steckel mill (reversing)
- Cold rolling
  - High-throughput mills (Sendzimir, reversing)
  - Heavy reduction
  - Fast speeds
- Annealing
  - Continuous process (strand)
  - Air anneal and descaling (pickling)
  - Hydrogen bright anneal
  - Vacuum anneal

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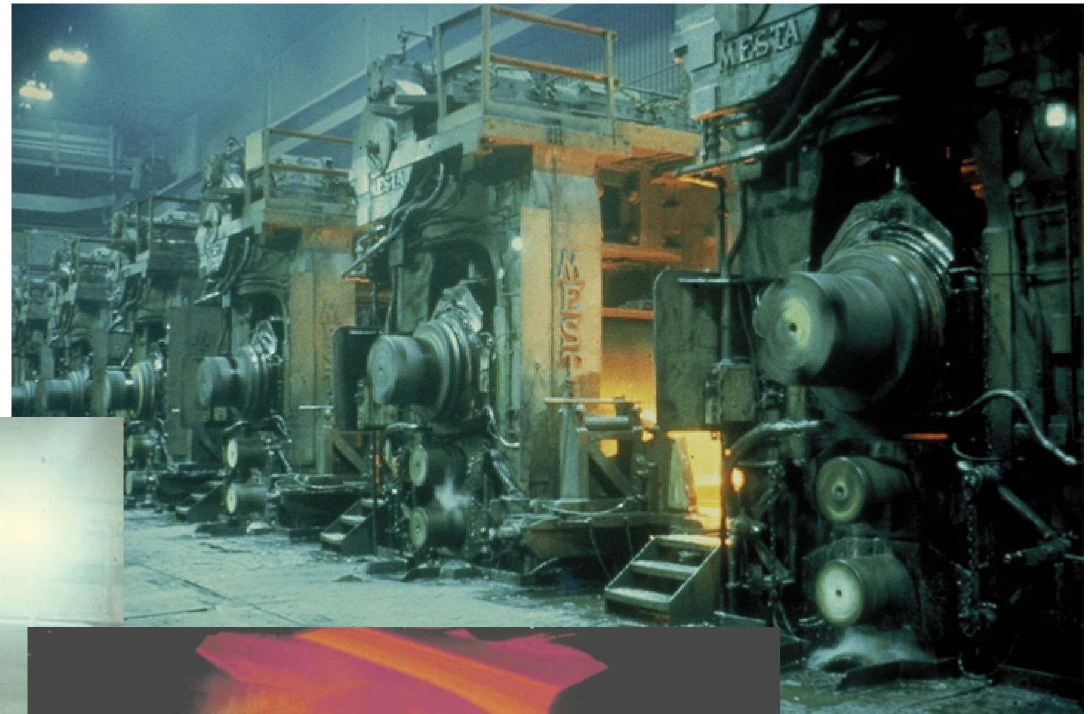
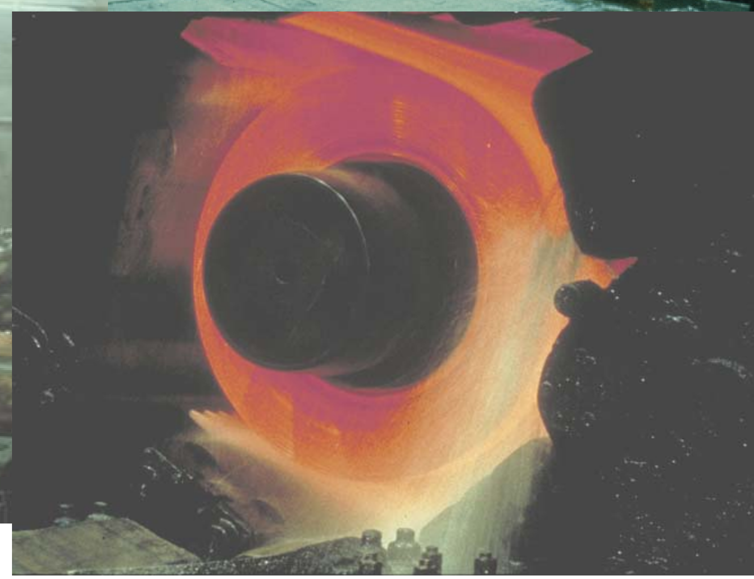
Hot Rolling





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Hot Rolling

- Hot workability range
  - Can be narrow for highly alloyed materials
  - Hot deformation testing to determine workability range
- Very strong alloys may be difficult to work
  - Powerful hot rolling mills
  - Smaller sizes
- Precipitation reactions (e.g. γ') make difficult coiling and uncoiling
  - Kinetic studies to determine precipitation behavior
  - Chemistry modifications
- Edge checking
  - Control of temperature uniformity

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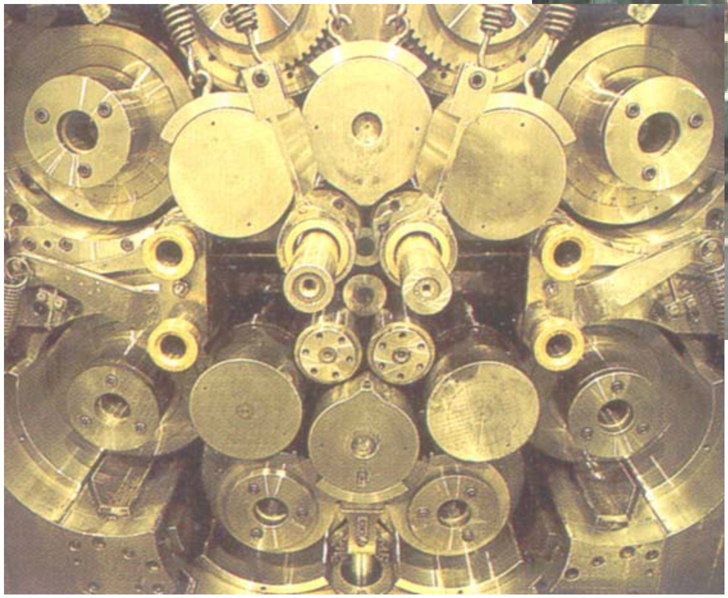
Cold Rolling



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Cold Rolling

- Poor rolling behavior
  - Brittleness
  - High work hardening rate
- Causes
  - Chemistry
  - Microstructure / phase balance
- Consequences
  - Numerous anneal cycles
  - Breakage / lower yield
- Potential Solutions
  - Minimize elements which impact rollability
  - Control phase balance
  - Lab rolling trials to establish process limits

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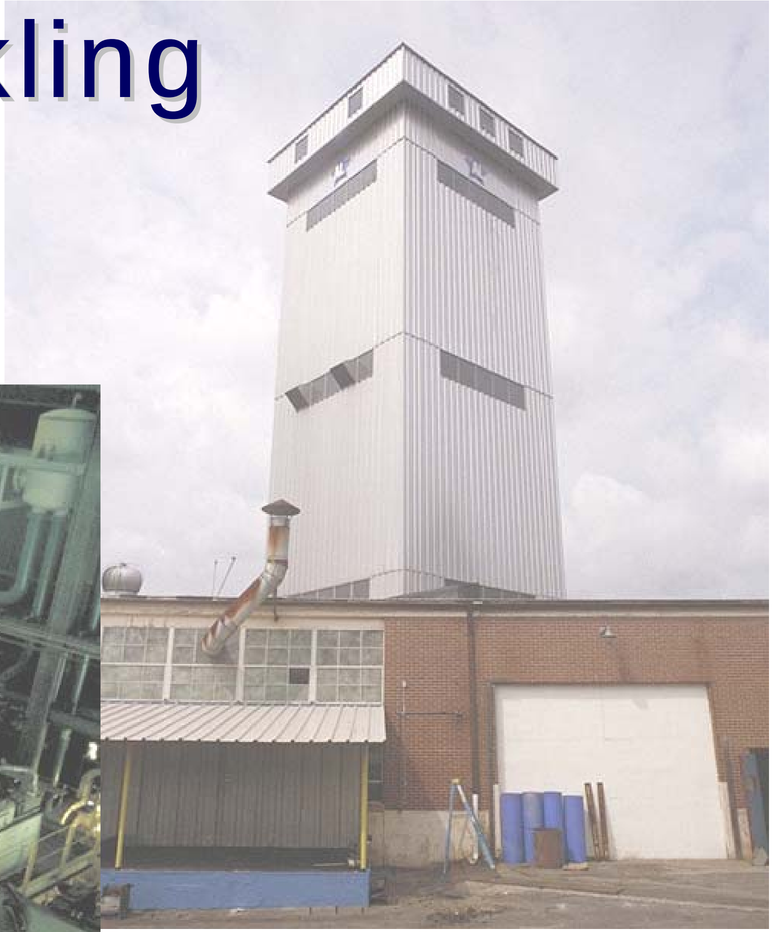
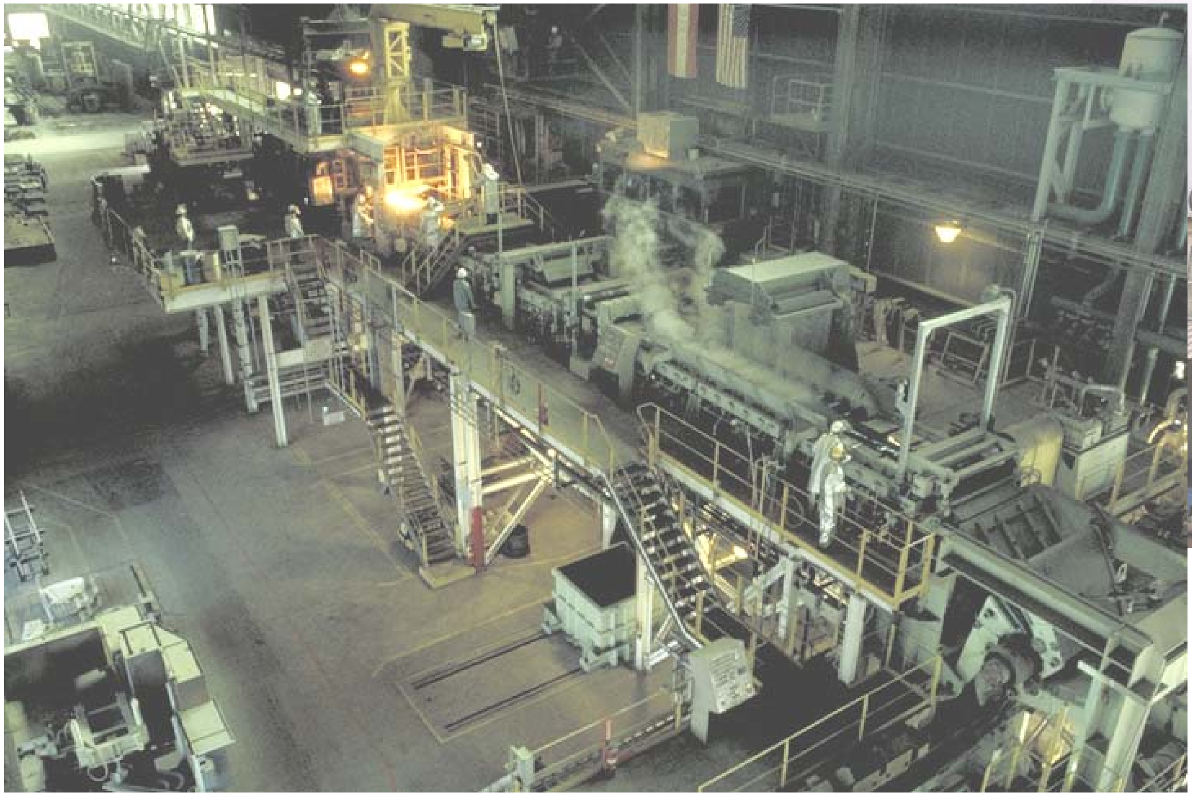
Annealing and Pickling





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Annealing and Pickling

- Critical factors
  - Grain size
  - Surface condition
    - Oxide removal
    - Removal of altered metal (e.g. Cr-depleted zone for stainless steel, alpha case layer for Ti)
- Potential solutions
  - Annealing cycle trials (Gleeble)
  - Lab-scale pickling trials
  - Corrosion testing
  - Oxidation testing
  - Welding trials

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Economics

- More expensive alloying additions
  - Nickel, molybdenum, cobalt
  - Rare earth elements
  - Precious metals
- Price volatility
  - Alloying additions
  - Base metals

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Economics

- Alloying additions which may necessitate advanced melting practices
  - Rare earth elements
  - Refractory metals
  - Volatile additions
  - Cleanliness / ultra-low residual element requirements
- Sole-purpose generally more expensive than multi-purpose alloys
- Best technical solution not always best commercial solution

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Economics

- When is the material cost critical?
  - Questionable
    - Prototypes / proof of concept
    - Critical performance requirements
  - Perhaps
    - Low volume production
    - Low quantity incorporation
  - Certainly
    - High volume production
    - High quantity incorporation

Selected Recent ATI Alloy Development Projects

- AL 2003™ alloy
  - Lean duplex stainless steel alloy
  - Balanced corrosion resistance and strength at relatively low cost (economic alternative to Types 316 and 317 stainless)
- ATI™ 425 alloy
  - Alloy titanium made by coil processing without anisotropy
  - Properties similar to Ti-6-4 at lower cost
- AL 347HP™ alloy
  - Existing austenitic stainless steel composition (UNS S34700)
  - Proprietary processing yields thirty percent improvement in creep strength
- Type 388 (ZeCor™ alloy)
  - High-silicon austenitic stainless steel
  - Resistance to hot, concentrated sulfuric acid at relatively low cost

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Example - AL 2003™ Alloy Development

- Development of a lean duplex (α-γ) stainless steel
  - Adequate corrosion resistance and mechanical properties
  - Improved weldability
  - Improved phase stability
  - Lower cost

  with respect to existing alloys
- Literature survey / IP review
- Selection of compositions
  - Thermo-Calc simulations
  - PRE_N, MD_{30}, FN, T_σ
- Melted numerous lab-scale heats
  - Processed to plate and sheet sizes
  - Corrosion, impact, tensile testing, microstructural evaluation; heat-treatment studies for sigma solvus and α-γ phase balance
- Selection of primary composition

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Example - AL 2003™ Alloy Development

- Melted several commercial-scale heats
  - Corrosion, impact, tensile testing
  - Microstructural evaluation
  - Welding trials
  - Modified practices and chemistry to optimize corrosion resistance and microstructure, phase balance, and mechanical properties
- Qualifications
  - Acquired UNS number (S32003)
  - ASTM approvals for plate, sheet, strip, pipe, and tubing
  - Working on NORSOK, ASME code qualification (requires three heats) and customer acceptance

Example - AL 347HP™ Alloy Development

- Existing alloy modified to meet need for higher creep strength at foil thickness (200 microns or less)
- Optimize NbC carbide particle distribution and grain size by controlling thermomechanical processing
- Proven in laboratory setting on small trial pieces (ORNL)
  - Examine different heat input levels
  - Varied time at temperature combinations
- Ten-foot sections of foil spliced into production continuous coil anneal lines
  - Examine different heat input levels
  - Vary furnace set points and line speeds
  - Translation of lab experiments to production practice
- Full production coils processed using new annealing cycle
- Verified at all stages with creep testing and metallography

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Summary

- Iron and nickel-base alloy design and development is a relatively mature science
- Helpful tools exist to aid in alloy development
- Transition from laboratory to practice is critical, complex, and often challenging

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Acknowledgements

- David Bergstrom, ATI Allegheny Ludlum
- John Dunn, ATI Allegheny Ludlum
- John Grubb, ATI Allegheny Ludlum
- Henry Lippard, ATI Allvac
- Tom Matway, ATI Allegheny Ludlum
- Charles Stinner, ATI Allegheny Ludlum
- Steve Washko, ATI Allegheny Ludlum
- Prabhakar Singh, PNNL