Alloy Development

James M. Rakowski
ATI Allegheny Ludlum
An Allegheny Technologies Company

SECA Core Technology Program
SOFC Interconnection Technology Workshop
Argonne National Laboratory
July 28, 2004
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
<table>
<thead>
<tr>
<th>Allegheny Technologies</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Materials</strong></td>
</tr>
<tr>
<td>Stainless steel, Ni-base alloys, Ti (CP and alloy), Co-base alloys, Zr, Hf, WC, +++</td>
</tr>
<tr>
<td><strong>Product Forms</strong></td>
</tr>
<tr>
<td>Sheet, Strip, Plate, Billet, Bar, Rod, Castings, Forgings, and Cutting Tools</td>
</tr>
<tr>
<td><strong>Sales Distribution</strong></td>
</tr>
<tr>
<td>US 77%</td>
</tr>
<tr>
<td>Europe 12%</td>
</tr>
<tr>
<td><strong>Primary Markets</strong></td>
</tr>
<tr>
<td>(2003 annual report)</td>
</tr>
<tr>
<td>Aerospace 18%</td>
</tr>
<tr>
<td>CPI / O&amp;G 10%</td>
</tr>
<tr>
<td>Automotive 12%</td>
</tr>
<tr>
<td>Appliance 10%</td>
</tr>
<tr>
<td>Power Gen 11%</td>
</tr>
<tr>
<td>Cutting Tools 10%</td>
</tr>
<tr>
<td><strong>ATI Operating Companies</strong></td>
</tr>
<tr>
<td>Allegheny Ludlum, Allvac, Wah Chang, Metalworking Products, Portland Forge, Casting Service</td>
</tr>
<tr>
<td><strong>ATI Joint Ventures</strong></td>
</tr>
<tr>
<td>STAL, UNITI</td>
</tr>
</tbody>
</table>
# ATI Allegheny Ludlum Products

## Stainless Steels and Specialty Alloys

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

## Nickel-Base Alloys

<table>
<thead>
<tr>
<th>Grade</th>
<th>Property</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat-Resistant Grades</td>
<td>Corrosion-Resistant Grades</td>
</tr>
<tr>
<td>AL800™/AL800H™, AL825™, AL600™, AL601™ alloys</td>
<td>AL22™, AL276™, ALLCOR®, AL400™ alloys</td>
</tr>
<tr>
<td>ALTEMP® 625, ALTEMP® 718, ALTEMP® HX, ALTEMP® 263 alloys, X-750 alloy</td>
<td></td>
</tr>
</tbody>
</table>

™ Trademarks of ATI Properties, Inc.
® Registered Trademarks of ATI Properties, Inc.
ATI Allegheny Ludlum Technical Center
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
Technical Center
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$_2$O$_3$, Al$_2$O$_3$, SiO$_2$
  – Choice depends on application
    • Temperature
    • Environment
    • Strength requirements
  – Incorporate sufficient amount to form and maintain an external oxide scale
  – Most wrought heat-resistant alloys rely on chromium oxide

• Required operating lifetime
• Cost
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
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
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
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
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.
Constitutive Expressions

**Ferrite Number (δ ferrite)**

\[ FN = 3.53(C_{eq}) - 2.61(N_{eq}) - 30.03 \]

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

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

**Electron Vacancy (TCP phases)**


**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)**

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

**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.
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

Al–0.23Cr–1.6Cu–0.5Fe–2.5Mg–0.3Mn–0.4Si–5.6Zn wt% (Balance: Cu)

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
Computational Design

TTT NiFe 718 superalloy

CCT NiFe 718 superalloy

Diagrams from JMat-Pro example manual
IN939 nickel superalloy heat treated at 720C
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
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
Lifetime Map for Metal Foil

- **Yield Stress Curve**
- **100,000 hour life**
  - No breakaway oxidation
  - 1% max creep

**Oxidation Limits**
(expanded from 10,000 hour tests)

- 1300°F test
- 1400°F test

**Graph Details**

- **Operating Stress (ksi)**
  - 60
  - 40
  - 20
  - 10
  - 0

- **Operating Temperature (°F)**
  - 0
  - 250
  - 500
  - 750
  - 1000
  - 1250
  - 1500
Lifetime Map for Metal Foil

60,000 hour design lifetime
maximum 1% creep
no breakaway oxidation
(based on expansion of 1300°F test data)

- Type 347
- AL 20-25+Nb™ Alloy
- ALTEMP® 625 alloy

Operating Stress (ksi)

Operating Temperature (°F)
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
Factorial Analysis

- Simplest example is a two factor DOE experiment

- Diagram illustrating the four experiments:
  - A- B+
  - A+ B-
  - A- B-
  - A+ B+

- Factors (A, B) with levels (+, -)
- Four experiments

+ A + B +
- A - B -
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

<table>
<thead>
<tr>
<th>number of factors (k)</th>
<th>2 levels $2^k$</th>
<th>3 levels $3^k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>4</td>
<td>9</td>
</tr>
<tr>
<td>3</td>
<td>8</td>
<td>27</td>
</tr>
<tr>
<td>4</td>
<td>16</td>
<td>81</td>
</tr>
<tr>
<td>5</td>
<td>32</td>
<td>243</td>
</tr>
<tr>
<td>6</td>
<td>64</td>
<td>729</td>
</tr>
<tr>
<td>7</td>
<td>128</td>
<td>2,187</td>
</tr>
<tr>
<td>8</td>
<td>256</td>
<td>6,561</td>
</tr>
</tbody>
</table>
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 (3rd 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
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
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
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
Melting
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)
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
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
Hot Rolling
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. $\gamma'$) make difficult coiling and uncoiling
  – Kinetic studies to determine precipitation behavior
  – Chemistry modifications

• Edge checking
  – Control of temperature uniformity
Cold Rolling
Cold Rolling

- Poor rolling behavior
  - Britteness
  - 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
Annealing and Pickling
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
Economics

- More expensive alloying additions
  - Nickel, molybdenum, cobalt
  - Rare earth elements
  - Precious metals

- Price volatility
  - Alloying additions
  - Base metals
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
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

™ Trademark of ATI Properties, Inc.
ZeCor is a trademark of Monsanto Industries LLC
Example - AL 2003™ Alloy Development

- Development of a lean duplex ($\alpha$-$\gamma$) stainless steel
  - Adequate corrosion resistance and mechanical properties
  - Improved weldability
  - Improved phase stability
  - Lower cost

- Literature survey / IP review

- Selection of compositions
  - Thermo-Calc simulations
  - PRE$_N$, MD$_{30}$, FN, T$_\sigma$

- Melted numerous lab-scale heats
  - Processed to plate and sheet sizes
  - Corrosion, impact, tensile testing, microstructural evaluation; heat-treatment studies for sigma solvus and $\alpha$-$\gamma$ phase balance

- Selection of primary composition
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
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
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