Specialty Metals Production
Considerations for SOFC

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Introduction

- Specialty metals industry
- Specialty metals products and forms
- Processing of specialty metals
- Product development considerations
- Raw material challenges
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- Specialty metals industry
- Specialty metals products and forms
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- Raw material challenges

Focus on high volume production & low cost
Linking SOFC system designer with material designer
Specialty Metals Industry

- US consumption of stainless steel (all product forms) was 2.5 million tons in 2004*

- ATI Allegheny Ludlum produces over 700,000 tons per year of flat-rolled products;
  
  stainless steel, specialty stainless, nickel-base alloys, titanium, and other specialty metals such as multi-layered clad products

* SSINA news release, 03/18/2005
www.ssina.com
Specialty Metals by Composition

• Ferritic stainless steels \((Fe-Cr)\)
• Austenitic stainless steels \((Fe-Ni-Cr)\)
• PH stainless steels \((Fe-Ni-Cr)\)
• Iron-base superalloys \((Fe-Ni-Cr)\)
• Nickel-base superalloys \((Ni-Cr-Fe)\)
• Cobalt-base superalloys \((Co-Cr-Ni)\)
• Reactive metals
  – Titanium
  – Zirconium
  – Niobium
  – Hafnium
  – Tantalum
Specialty Metals by Composition

- Interconnects (ferritics, Ni alloys)
- Heat Exchangers (specialty steels, Ni alloys)
- Reformers (Ni alloys, etc.)
- Other Balance of Plant
Specialty Metals by Composition

- Interconnects
- Heat Exchangers
- Reformers
- Other Balance of Plant

The commercially competitive SOFC system would likely require a combination of high temperature specialty materials. Material selection would likely be driven by performance, cost, and material availability considerations.
Stainless Steels and Ni-Base Alloys

Austenite ($\gamma$) stabilized by C, N, Ni, Mn, Cu, Co

Ferrite ($\alpha$) stabilized by Al, Ti, V, Si, Cr, Mo, W, Ta

- Ferritic stainless steels
- Austenitic stainless steels
- Duplex stainless steels
- Nickel-base superalloys
Ferritic Stainless Steels

**AL444™ AL436S™ stainless steels**

"superferritics"  
*E-BRITE® alloy, AL 29-4C® alloy, SEA-CURE® alloy*

**Mo**

↑ strength, creep resistance  
↑ oxidation, corrosion resistance  
↓ stability  
Potential catastrophic oxidation

**Fe-Cr**

Type 409

↑↑ oxidation resistance  
↓ manufacturability  

_AL 409ALMZ™_  
*(external coating)_  
_ALFA-I®, ALFA-II® alloys, FeCrAl alloys*

**Cr**

↑ strength, creep, oxidation, corrosion resistance  
↓ stability  
*Types 430, 446*

**AL439HP™, AL441HP™ stainless steels**

**Nb, Ti, Ta, W**

↑ strength, creep, corrosion resistance

_AL409HP™ stainless steel*

SOFC Interconnect Alloys

Typically tend to resemble relatively lean superferritic stainless steels with specific constraints on minor alloy chemistry

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Superalloys

Ni-Cr (γ phase)

Solid-solution and carbide-strengthened alloys
Cr, Co, Fe, Mo, Ta, W

Corrosion-resistant alloys
AL22™ Alloy, ALLCORR® Alloy

Heat and corrosion-resistant alloys
ALTEMP® 600, ALTEMP® 601, ALTEMP® 625, ALTEMP® HX Alloys

Precipitation strengthened alloys
Al + Ti (γ’ Ni₃Al phase)
ALTEMP® A286 Alloy (Fe-Ni)
ALTEMP® X-750, ALTEMP® 263 Alloys, Waspaloy (Ni)

Nb + Fe (γ” Ni₃Nb phase)
ALTEMP® 718 Alloy

SOFC Interconnect Alloys
Ni and Ni base alloys have shown promising surface properties. Issues exist relative to CTE and cost

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Specialty Metals by Product Form

• **Flat Products**
  - **Sheet**
    Typically < 3/16” thick and > 24” wide
  - **Strip**
    Typically < 3/16” thick and < 24” wide
  - **Precision Rolled Strip® Product**
    Typically < 0.015” and other specialized products at heavier gauges
    Produced to tight tolerances other restrictions, Foil typically < 0.005”
  - **Plate**
    Typically > 3/16” thick and > 10” wide

• **Long Products**
  bar, billet, rod

• **Others**
  pipe, tubing, wire castings, forgings, powder

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Primary Production Overview

Melting
argon-oxygen decarburization vessel

electric arc furnace

ingot casting

ingot heating (soaking pits)

hot rolling ingot to slab

blooming mill

shear

slabs

continuous casting

hot rolling slabs to bar

slab reheat

scale breaker

roughing mill

hot rolling bar to coil

six-stand hot strip mill

HRB coil
Coil Processing Overview

HRB coil → A&P → B&P → intermediate cold rolling → coil grinding → intermediate annealing

finish rolling: Tandem mill, 4-high reversing mill, Sendzimir mill

final annealing: Bright annealing, A&P

post-processing: coil grinding, temper rolling

package and ship: slit-to-width, cut-to-length
Melting

• Primary melting practices
  – EAF electric arc furnace
  – EAF/AOD argon oxygen decarburization
  – VIM vacuum induction melting

• Re-melting practices
  – ESR electro-slag remelt
  – VAR vacuum arc remelt

• Premium melting practices
  – EB-CHR electron beam
  – PAM plasma arc melting
EAF / AOD Steelmaking

• Vast majority of stainless steel is produced via EAF/AOD process

• Electric arc furnace (EAF)
  – Scrap steel charge melted via arc struck between metal and consumable graphite electrodes
  – Allows for versatile raw materials usage (computer modeling of composition and cost)
  – Resulting molten steel transferred via ladle to the AOD for refining
Electric Arc Furnace

ATI Allegheny Ludlum
Electric Furnace Shop - Brackenridge Works
Hot Metal Transfer

ATI Allegheny Ludlum
AOD Melt Shop - Brackenridge Works
AOD Refining

- Major breakthrough in stainless steel production (1970’s)
- Primarily a refining stage
- Permits the production of clean stainless steel low in carbon, sulfur (ppm level) from relatively impure raw materials
- Works with a charge of hot metal transferred from the EAF, scrap steel, and selected additions
Argon-Oxygen Decarburization

ATI Allegheny Ludlum
AOD Melt Shop - Brackenridge Works
AOD Refining Stages

• Gas blow
  – Mixture of Ar, O$_2$, N$_2$ injected into molten steel through submerged tuyeres
  – Carbon content lowered by oxidation
  – Final carbon content controlled primarily by chromium content (C and Cr at equilibrium)

• Deoxidation
  – Bubbles of inert gases tend to carry off dissolved oxygen
  – Increase (Ar,N$_2$):O$_2$ ratio as melting proceeds
  – Actively deoxidize using reactive additions (Al, Ti, Ca, Si)
AOD Refining Stages

• Slag reduction
  – Metallic elements (Cr, Mo, Ni) tend to oxidize and partition to slag
  – Si, Al added to reduce these oxides to near 100% recovery

• Chemical analysis
  – On-line during melting
  – Allows for late corrections to alloy chemistry

• Tapping

• Ladle stirring and *late additions* of highly reactive alloying elements
Alternative Primary Melting Methods

• Vacuum induction melting (VIM) (Ni, Co)
  – Induction melting in a refractory crucible
  – Poured into an ingot mold
  – Used for high-quality, clean melting of alloys containing reactive additions

• Plasma arc melting (PAM) (Ti)
  – Melting in an inert gas under an electric arc from a non-consumable electrode
  – Melts a wide variety of feedstock forms

• Electron beam cold hearth melting (Ti)
  – Material melted by electron beams
  – Melts a wide variety of feedstock
  – Long residence time and bath geometry contribute to removal of LDI and HDI
Remelting

• Higher alloy-content materials prone to segregation
• Second and possibly third melt cycle used to homogenize alloys prone to segregation and/or improve cleanliness of finished ingot
• Primary ingot generally used as electrode
• Typically used for critical quality parts (rotating components; jet engines, pharmaceutical, etc.)
• Process control (e.g. melt rate, temperature profile) critical to achieving desired end result
Electroslag Remelting (ESR)

- Air melting under a slag blanket
- Electrode typically positioned above a fixed, water cooled copper mold
- Melt zone separated from solid electrode by molten slag blanket
- Melting proceeds by passing electric current through the slag blanket between the solid electrode and the molten pool
- Molten metal droplets pass through the slag, resulting in refinement and inclusion control
Vacuum Arc Remelting (VAR)

- Electrode typically positioned above a fixed, water cooled copper mold
- Melting proceeds by striking an arc between the solid electrode and the molten pool
- Can use a fabricated electrode rather than a solid ingot (Ti, Zr)
Casting

- Hot metal is solidified in a controlled manner into a desired shape

- Continuous casting
  - High-aspect ratio single strand cast in a fixed mold with water-cooled oscillating sides
  - Mold fed from above by a tundish
  - Enables several melt heats of continuous casting

- Ingot casting
  - Several large low-aspect pieces cast in removable molds
  - Bottom poured from ladle into a series of runners
  - Only used when concasting is not practical or technically feasible
  - Generally lower yield than concasting
Continuous Casting

ATI Allegheny Ludlum
Continuous Caster - Brackenridge Works
Ingot Casting

ATI Allegheny Ludlum - Brackenridge Works
Hot Rolling

- Ingots are reheated and bloomed to slab
- Slabs are reheated and rolled to bar
- Bar is fed directly to a hot rolling mill
- Types of hot rolling mills
  - Continuous mill (hot strip mill)
  - Reversing mill
  - Steckel mill (reversing mill with integral coil heating stations on either side)
Hot Rolling

ATI Allegheny Ludlum
Hot Strip Mill - Brackenridge Works
Cold Rolling

- Reversing mills
- Sendzimir mill
  - “Z” - mill
  - Small diameter work rolls surrounded by larger back-up rolls
  - Coiling stands provide tension
  - Large reductions possible on strong materials
  - Active shape and gauge control
  - Material can be produced as wide as 60” and as thin as 0.0007” (18 microns)
Cold Rolling
Annealing

- **Continuous process**
  - “Strand” annealing
  - End of one coil joined to start of next
  - Material hangs free in furnace (catermory)
  - Highest throughput

- **Batch process**
  - Box / bell annealing
  - Typically used for long exposures in controlled atmosphere
  - Entire coil annealed as a whole

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 Allegheny Technologies
Annealing

- **Air annealing**
  - Strip tends to oxidize
  - Followed by descaling treatments
  - Heavy gauge products

- **Reactive / inert atmospheres (bright anneal)**
  - Hydrogen
  - Cracked ammonia
  - Nitrogen
  - Endothermic / exothermic gases
  - Light gauge stainless and alloy products

- **Vacuum annealing**
  - Typically a batch process
  - Generally used for alloys incompatible with bright annealing (e.g. Ti)
Annealing

ATI Allegheny Ludlum
Anneal and Pickle Line - Leechburg Works

ATI Allegheny Rodney
Bright Anneal
Waterbury Works
Slitting

- Coils cut to desired width using circular slitting knives with very tight tolerances
- Widths controlled by building up knives and spacers on an arbor
- Edge shape and burr controlled by slitting and can be altered by dressing
- Slit mults can be wrapped around a spool (wide) or oscillate-wound (narrow)
Slitting
Optimal Production Process

- Lowest cost to meet application requirements
- Highest yield and material availability
- Production flexibility
- Low Raw Material Volatility
Product Development Process

- Technical Review & Initial Specification
- Small Lot Production & Evaluation
- Pilot Production Scale Manufacturing
- Product Evaluation
- Process Optimization
- Flow Path & Supply Chain Definition

ATI Allegheny Ludlum
Allegheny Technologies
Product Development Process

- Technical Review & Initial Specification
- Small Lot Production & Evaluation
Product Development Process

- Product Evaluation
- Process Optimization
Optimal Production Process

Air Melting
- electric arc furnace
- argon-oxygen decarburization vessel
- continuous casting
  - slabs

hot rolling slabs to bar
- slab reheat
- scale breaker
- roughing mill

hot rolling bar to coil
- six-stand hot strip mill
- HRB coil

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Allegheny Technologies
Optimal Production Process

HRB coil → conditioning → B&P → intermediate cold rolling → intermediate annealing

finish rolling → final annealing → Sendzimir mill → Bright annealing → package and ship → slit-to-width
Raw Material Challenges

LME NICKEL PRICE ($/lb)
1/01 through 5/05

Monthly Average Price

Average Price

ATI Allegheny Ludlum
Allegheny Technologies
Raw Material Challenges

MOLYBDENUM PRICE ($/lb)
1/01 through 5/05

Monthly Average Price

Average Price
Trigger

$0.00
$4.00
$8.00
$12.00
$16.00
$20.00
$24.00
$28.00
$32.00
$36.00

1/1/2001
5/1/2001
9/1/2001
1/1/2002
5/1/2002
9/1/2002
1/1/2003
5/1/2003
9/1/2003
1/1/2004
5/1/2004
9/1/2004
1/1/2005
5/1/2005
Raw Material Challenges

FerroTitanium Price ($/lb)
9/04 through 5/05

Monthly Average Price

Average Price


$2.00 $4.00 $6.00 $8.00 $10.00 $12.00 $14.00 $16.00
Summary

- Integrated SOFC Systems are likely to Contain a Wide Spectrum of Specialty Metals
- Those Metals will be Tailored to the Specific Application Based on Performance and Cost
- Specialty Materials Provider can Further Benefit the SOFC System Developer by Acting as a Technology Resource capable of Product Development, Application Support as well as Full Scale Production and Supply
- Across a Wide Range of Specialty Materials