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

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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

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* 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
  - Niobium
  - Tantalum
  - Zirconium
  - Hafnium

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Specialty Metals by Composition

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

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Specialty Metals by Composition

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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

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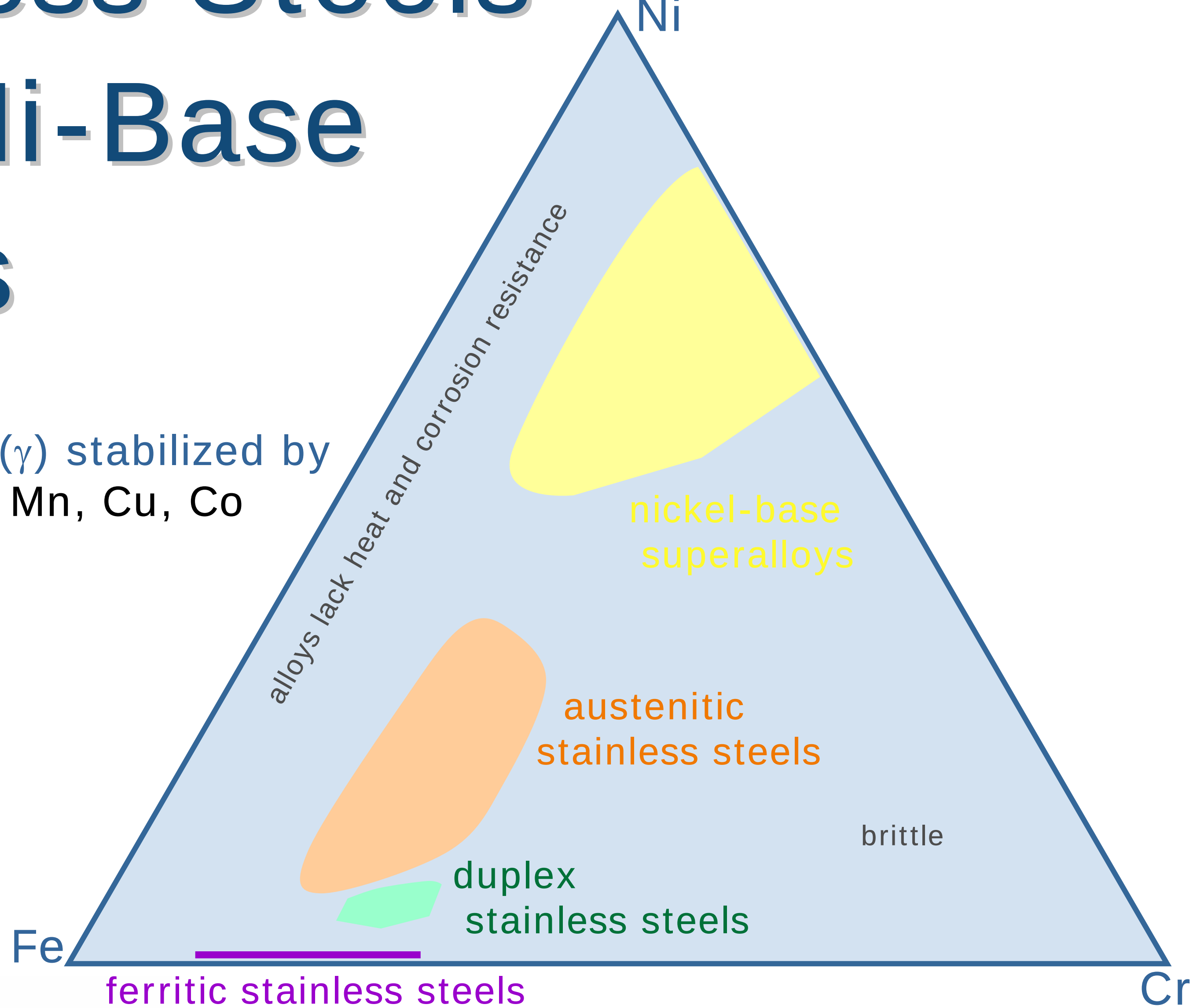
Stainless Steels and Ni-Base Alloys



Austenite (γ) stabilized by
C, **N**, Ni, Mn, Cu, Co

Ferrite (α) stabilized by
Al, Ti, V, Si, Cr, Mo, W, Ta

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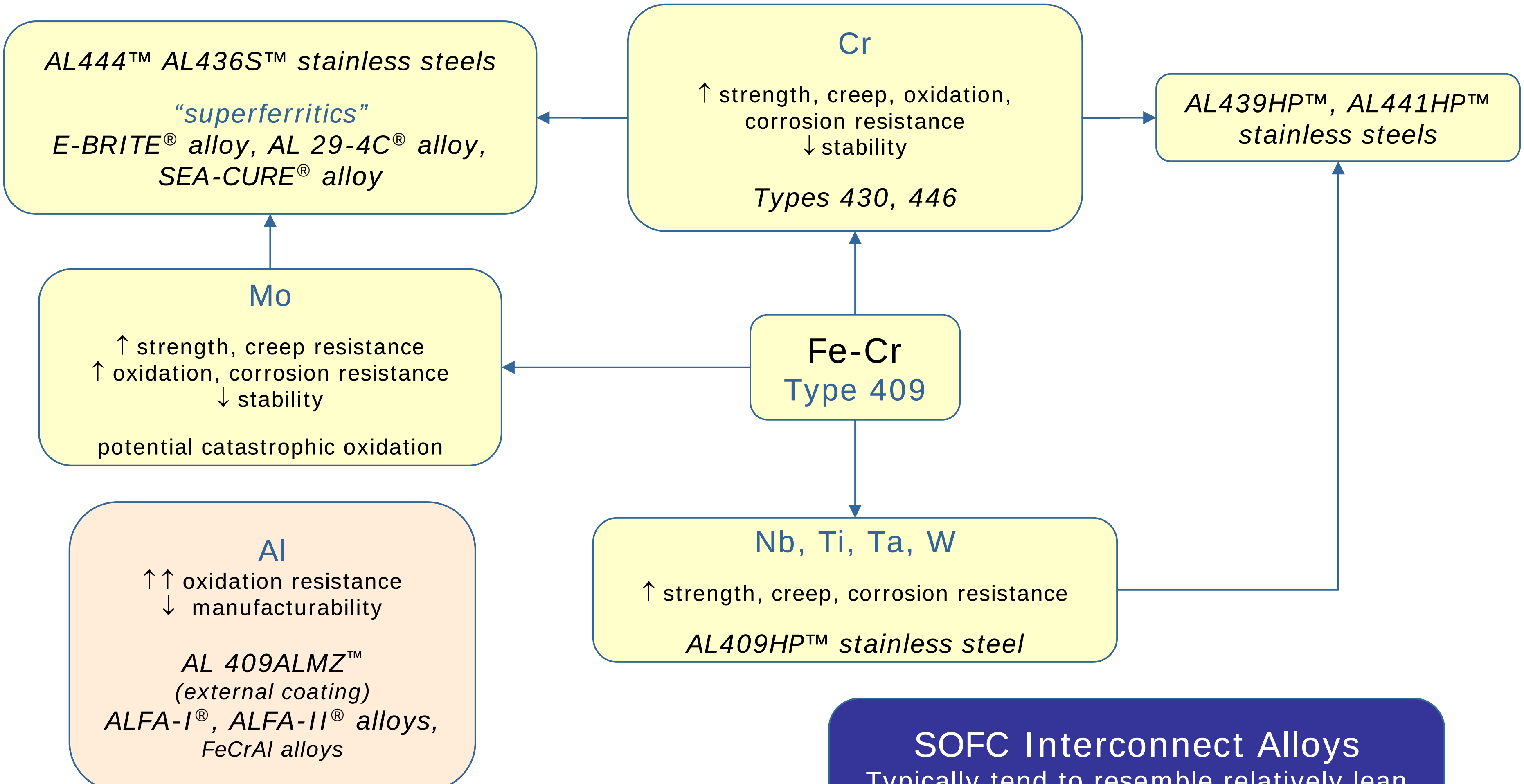
Ferritic Stainless Steels



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' Ni_3Al phase)

ALTEMP® A286 Alloy (Fe-Ni)

ALTEMP® X–750, ALTEMP® 263 Alloys, Waspaloy (Ni)

Nb + Fe (γ'' Ni_3Nb phase)

ALTEMP® 718 Alloy

SOFC Interconnect Alloys

Ni and Ni base alloys have shown promising surface properties. Issues exists 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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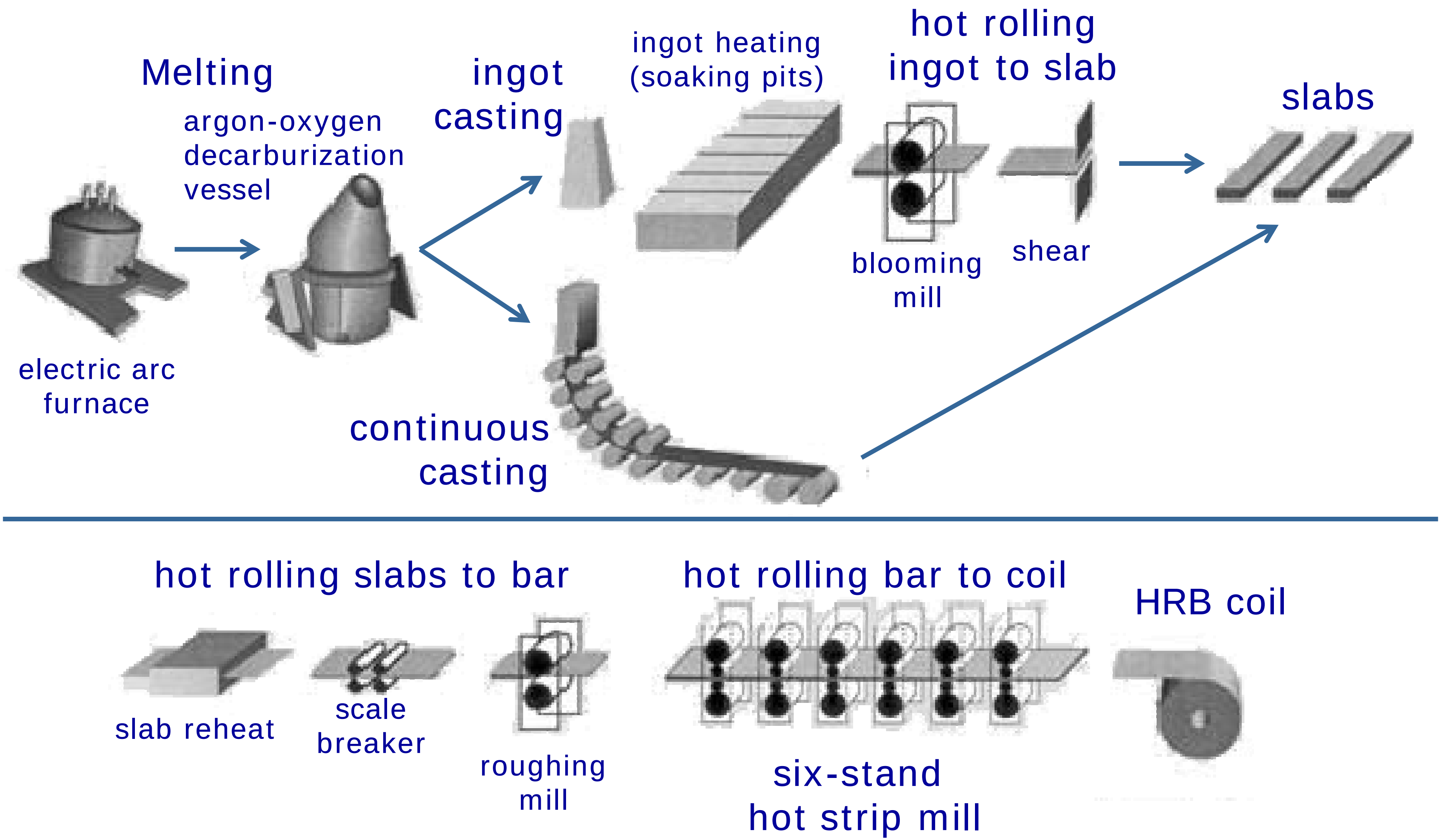
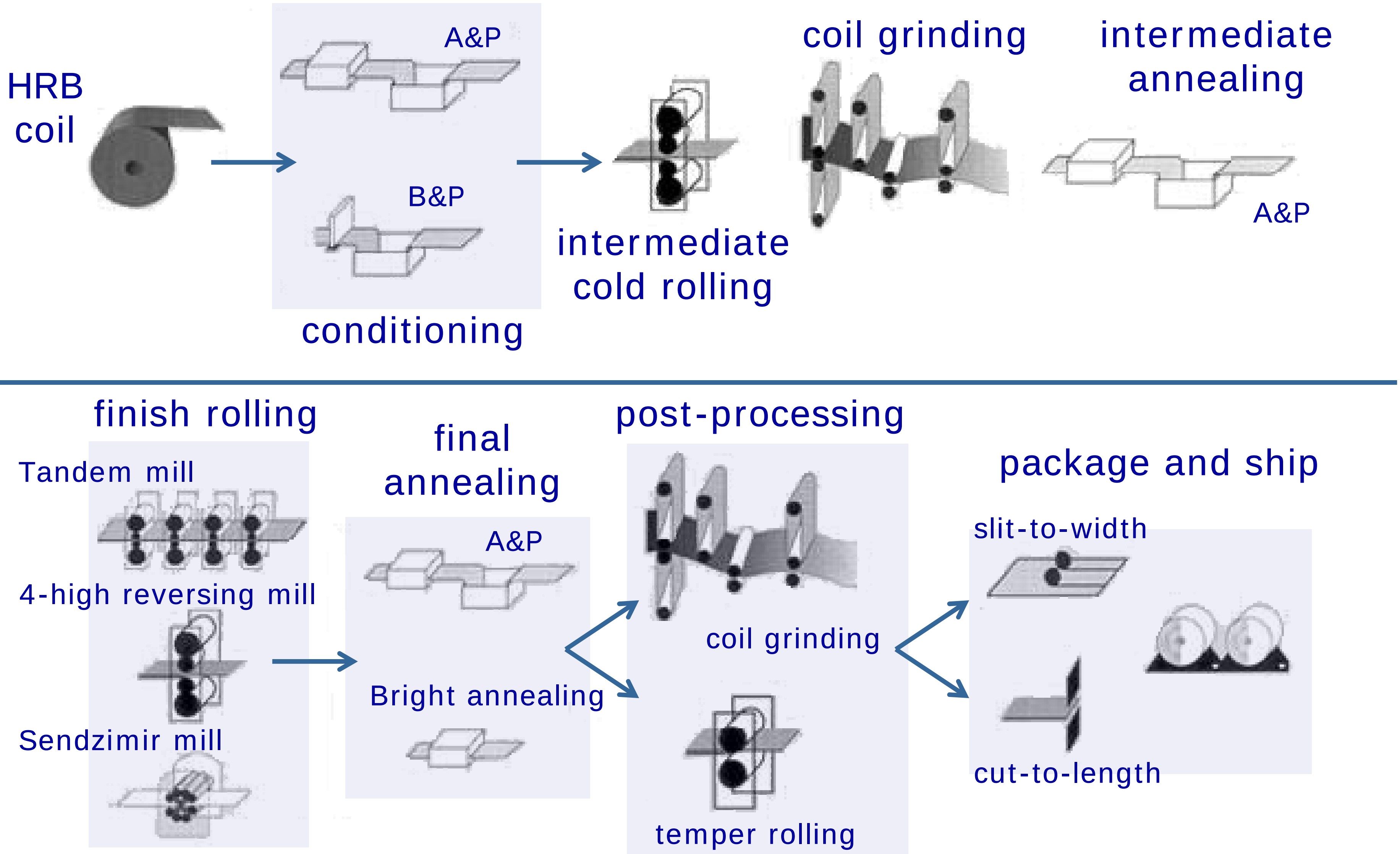
Primary Production Overview



Coil Processing Overview



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

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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

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Electric Arc Furnace

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Electric Furnace Shop - Brackenridge Works

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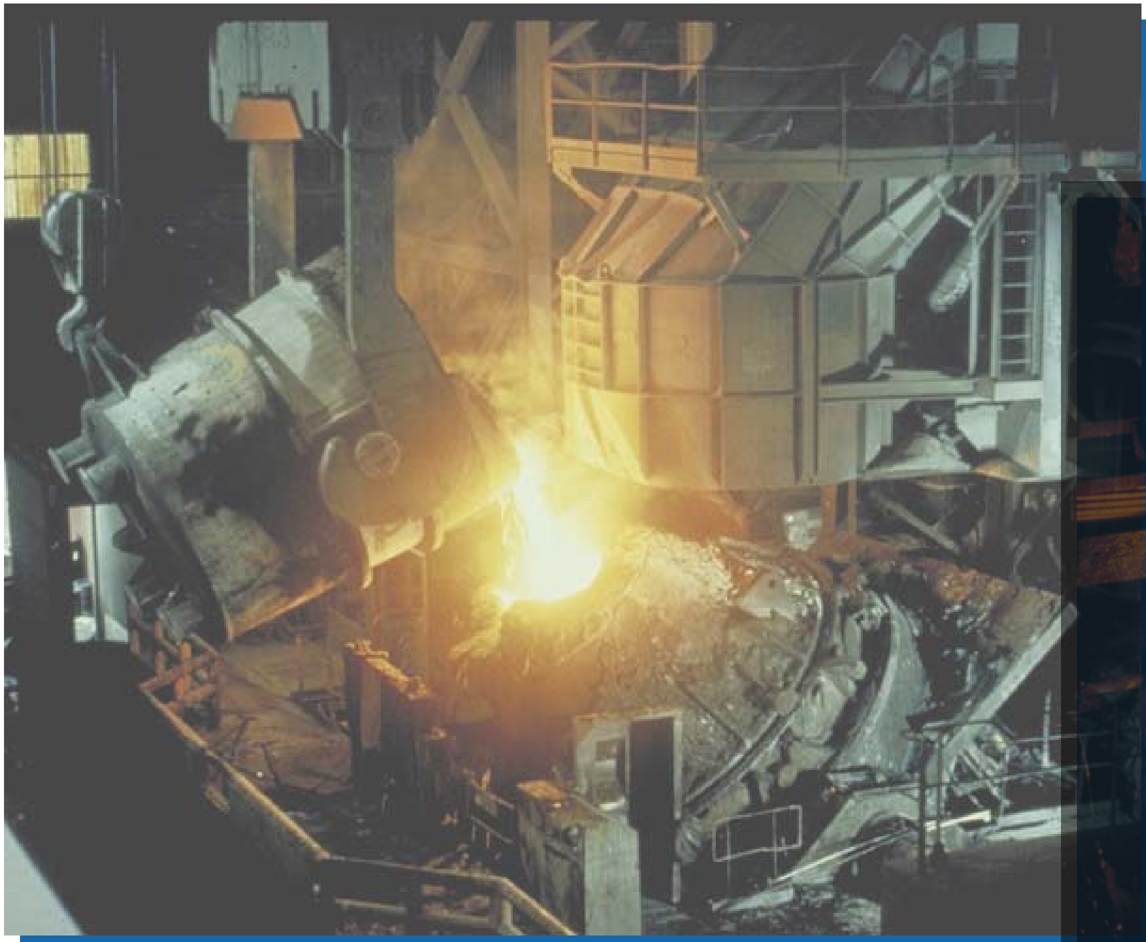
Hot Metal Transfer



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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

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Argon-Oxygen Decarburization

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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)

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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

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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

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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

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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

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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

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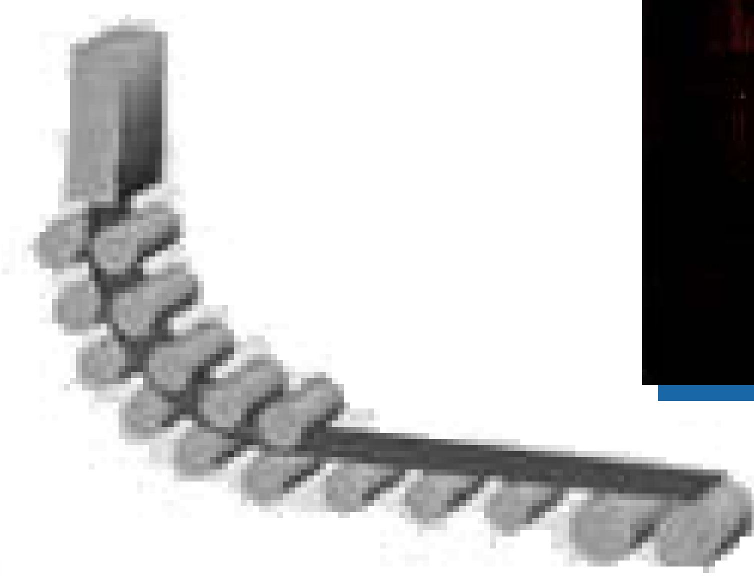
Continuous Casting



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Continuous Caster - Brackenridge Works

Ingot Casting

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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)

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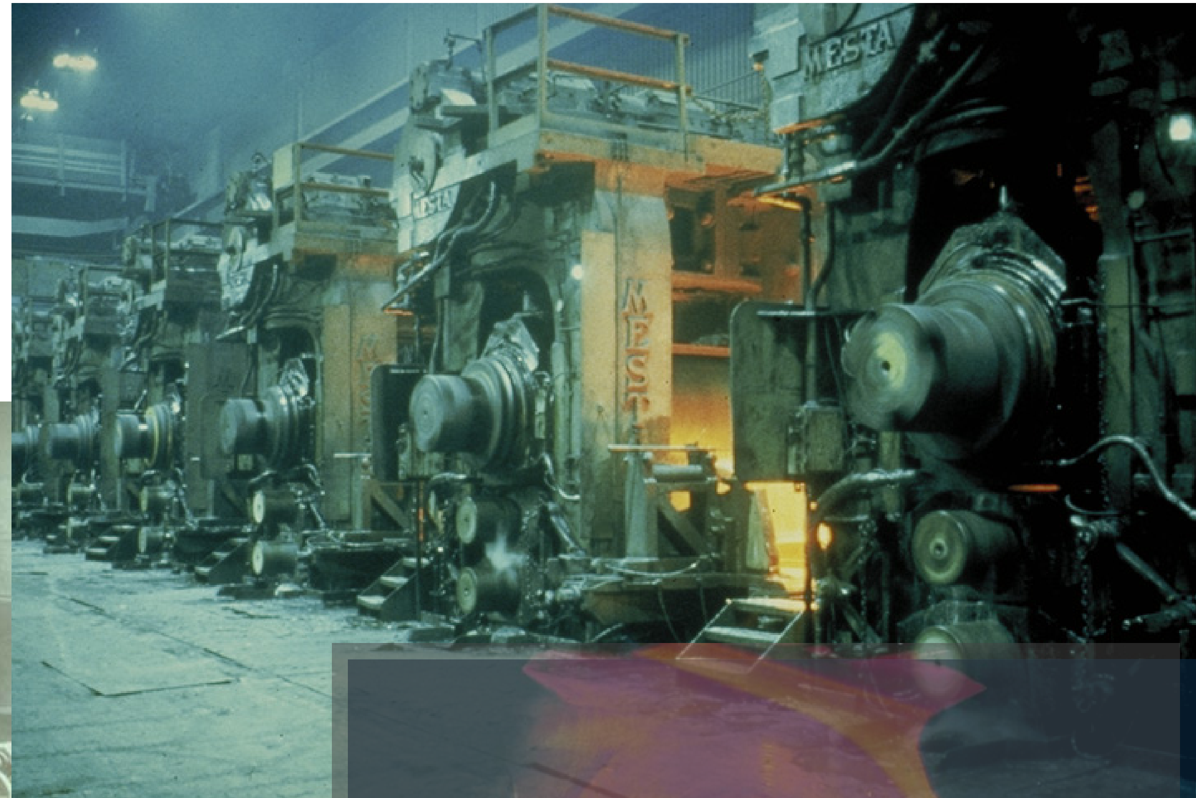
Hot Rolling



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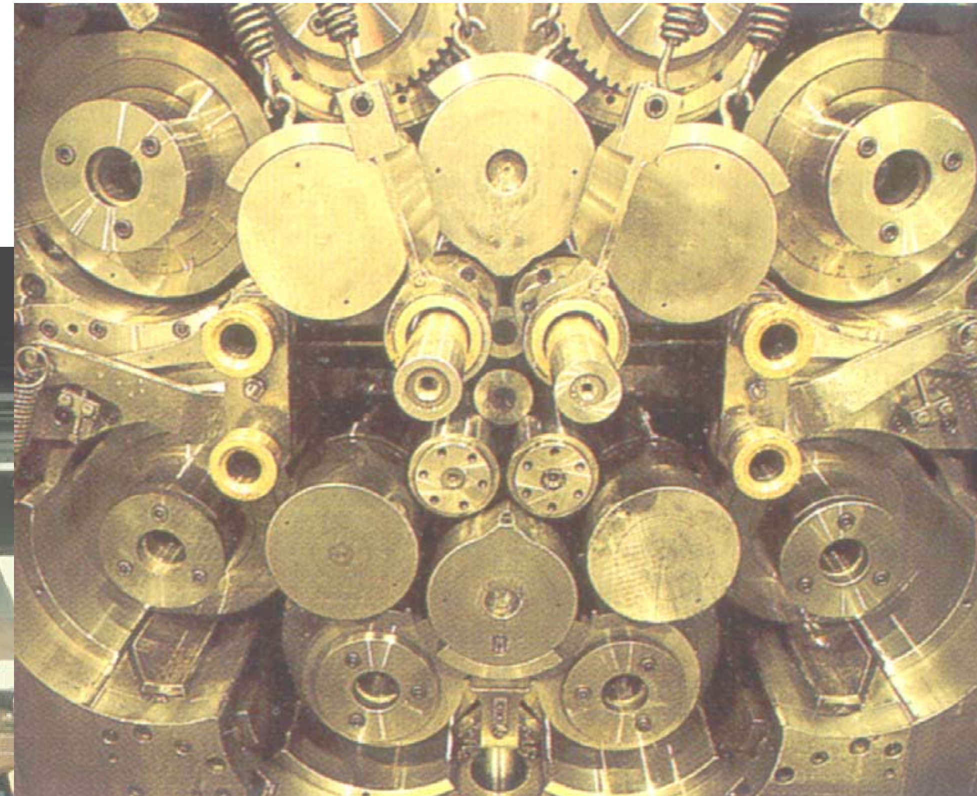
Hot Strip Mill - Brackenridge Works

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



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Annealing

- Continuous process
  - “Strand” annealing
  - End of one coil joined to start of next
  - Material hangs free in furnace (caternary)
  - Highest throughput
- Batch process
  - Box / bell annealing
  - Typically used for long exposures in controlled atmosphere
  - Entire coil annealed as a whole

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)

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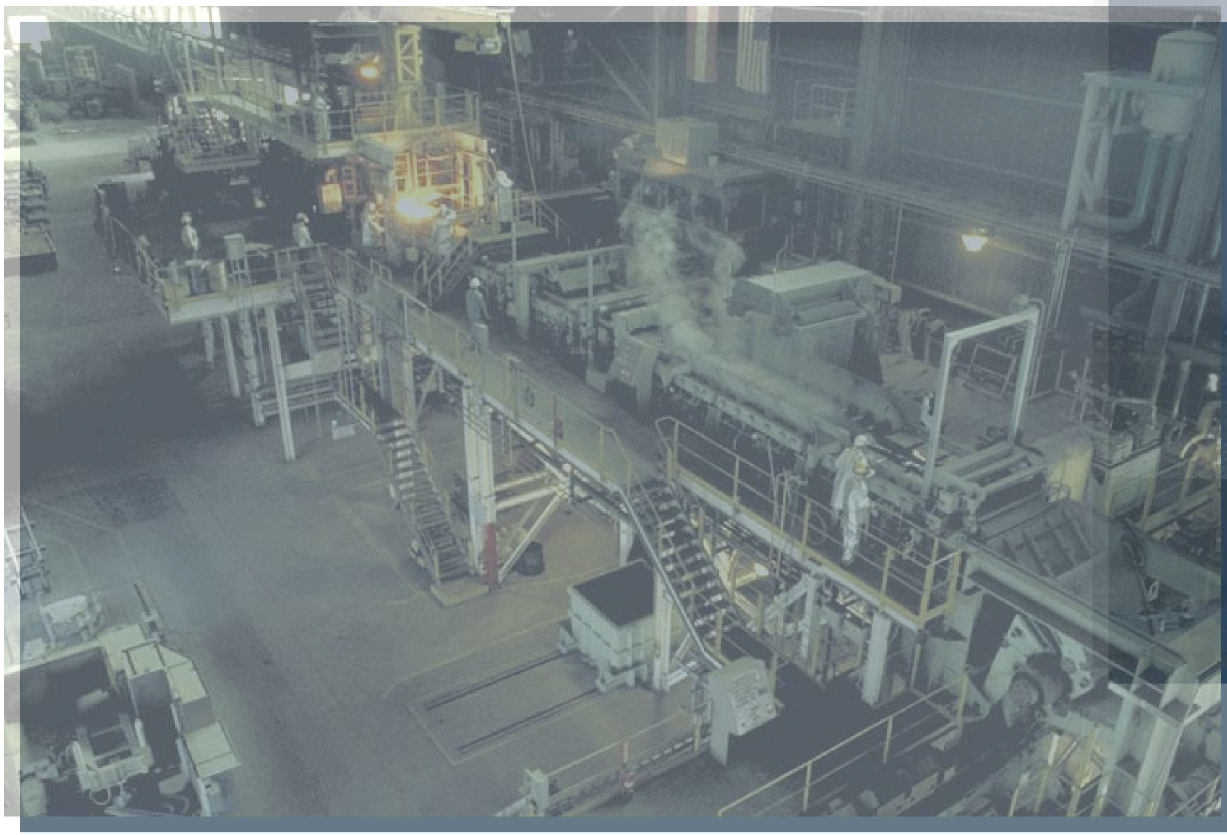
Annealing



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Anneal and Pickle Line - Leechburg Works

ATI Allegheny Rodney
Bright Anneal
Waterbury Works

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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)

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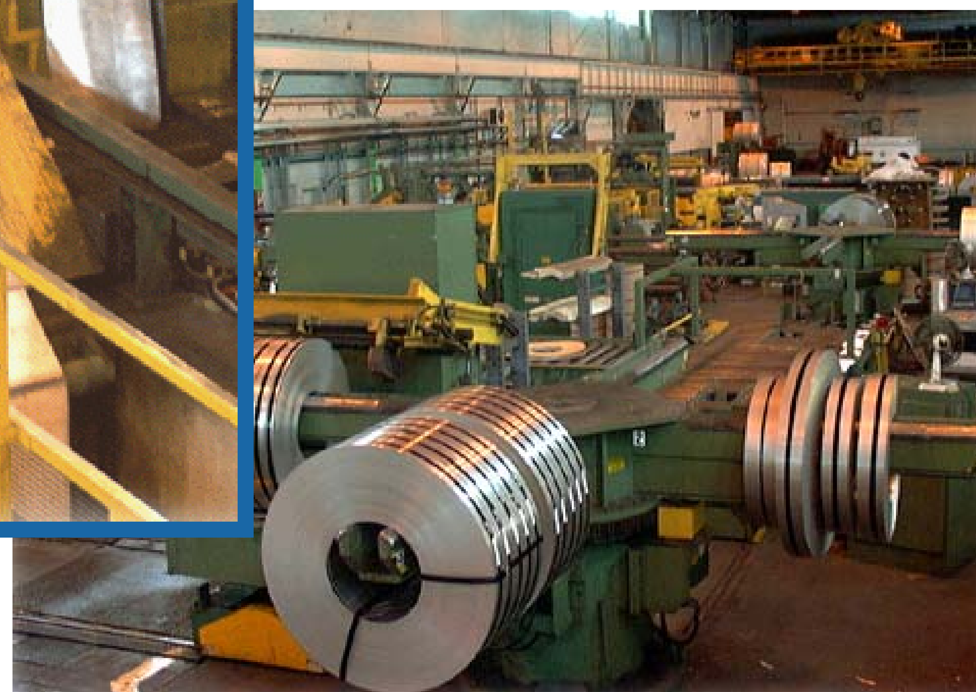
Slitting



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Optimal Production Process

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

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Product Development Process

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

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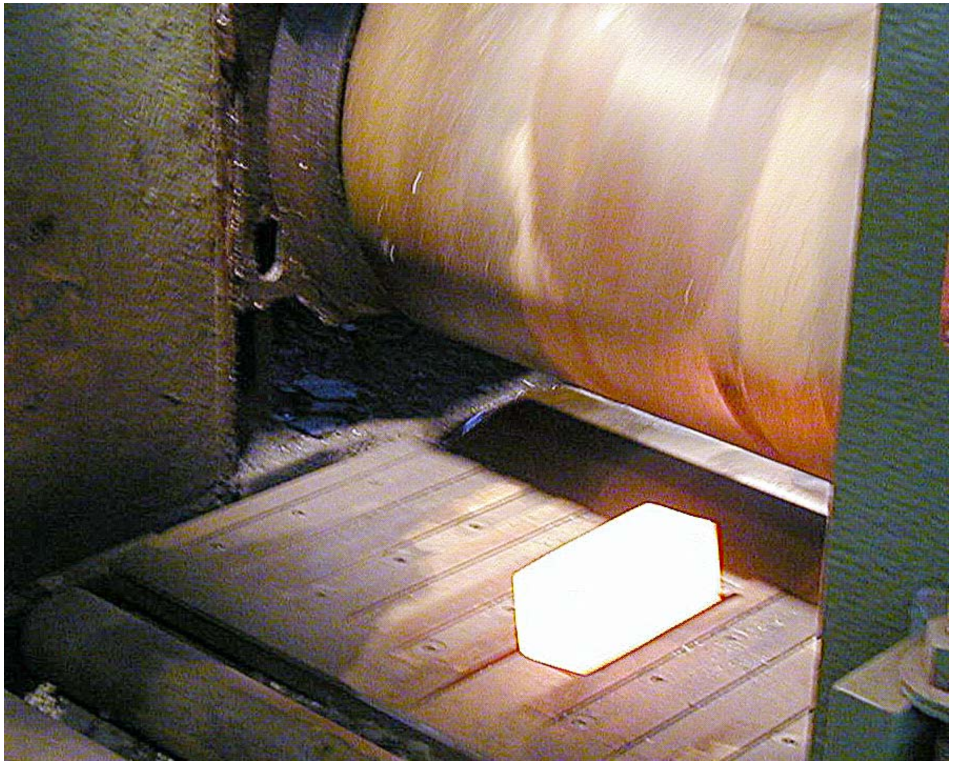

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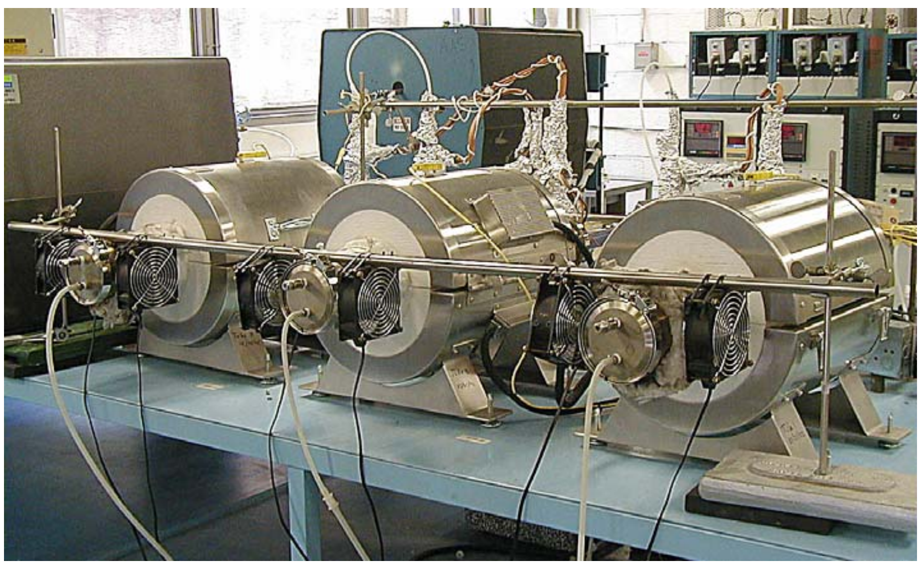

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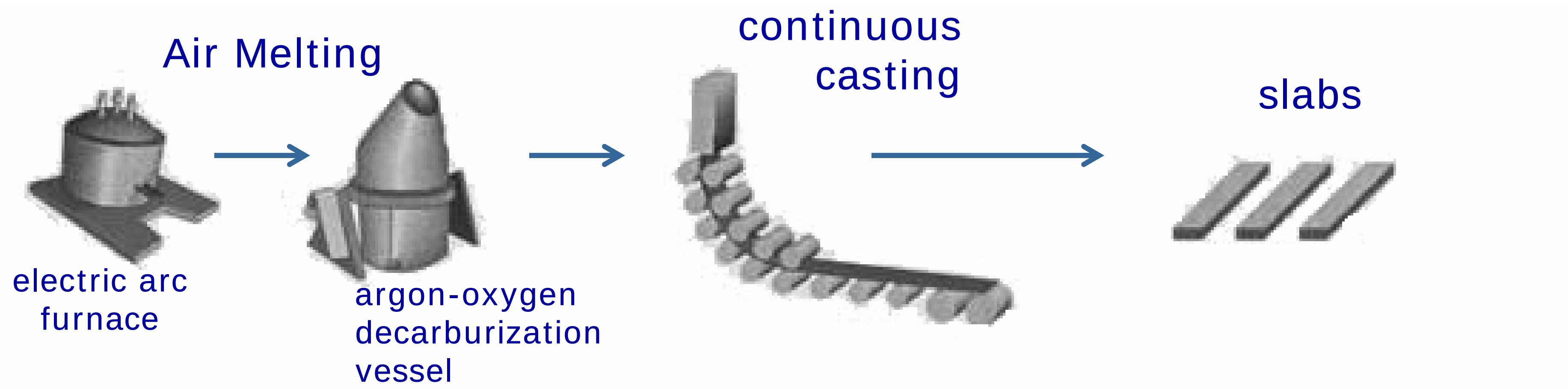
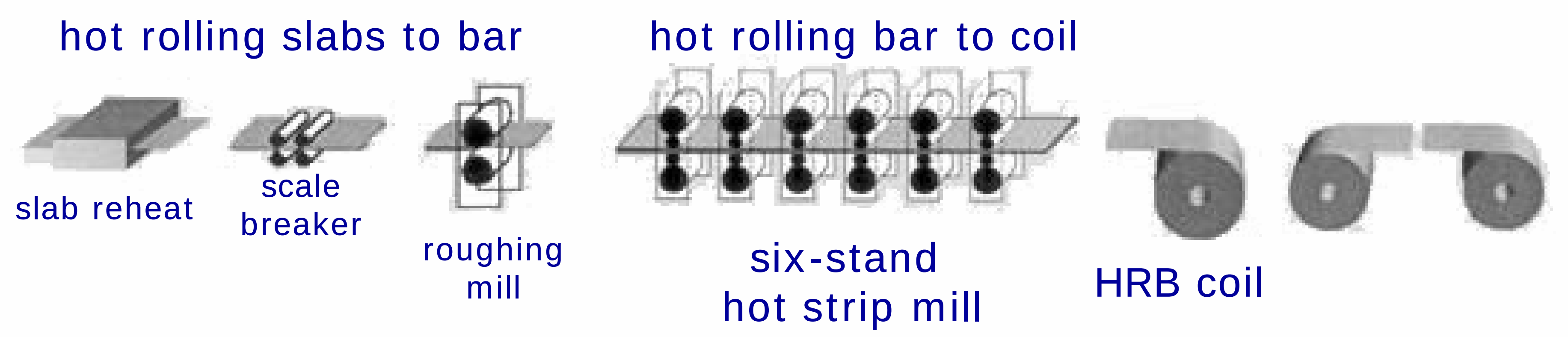
Optimal Production Process





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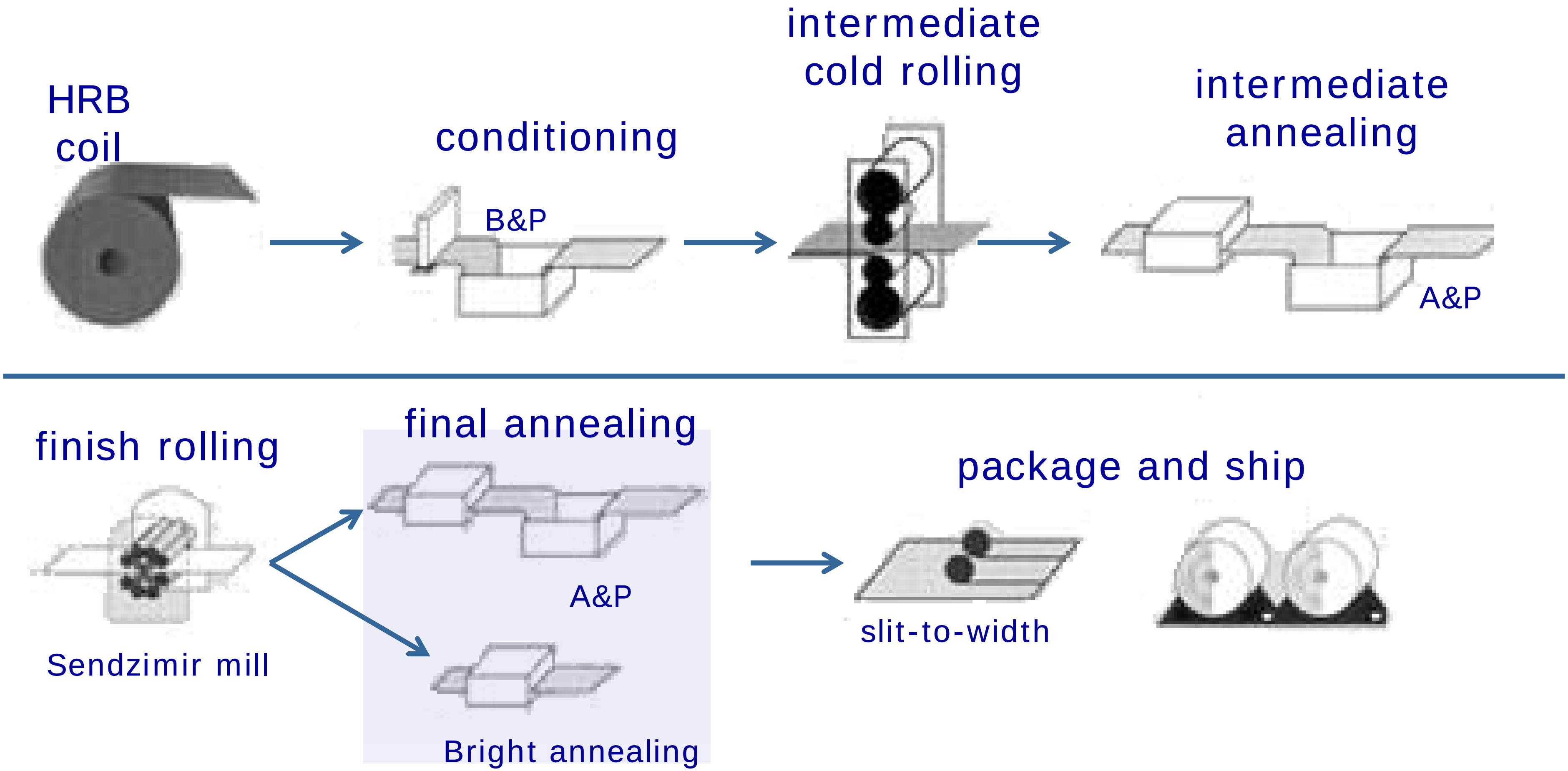
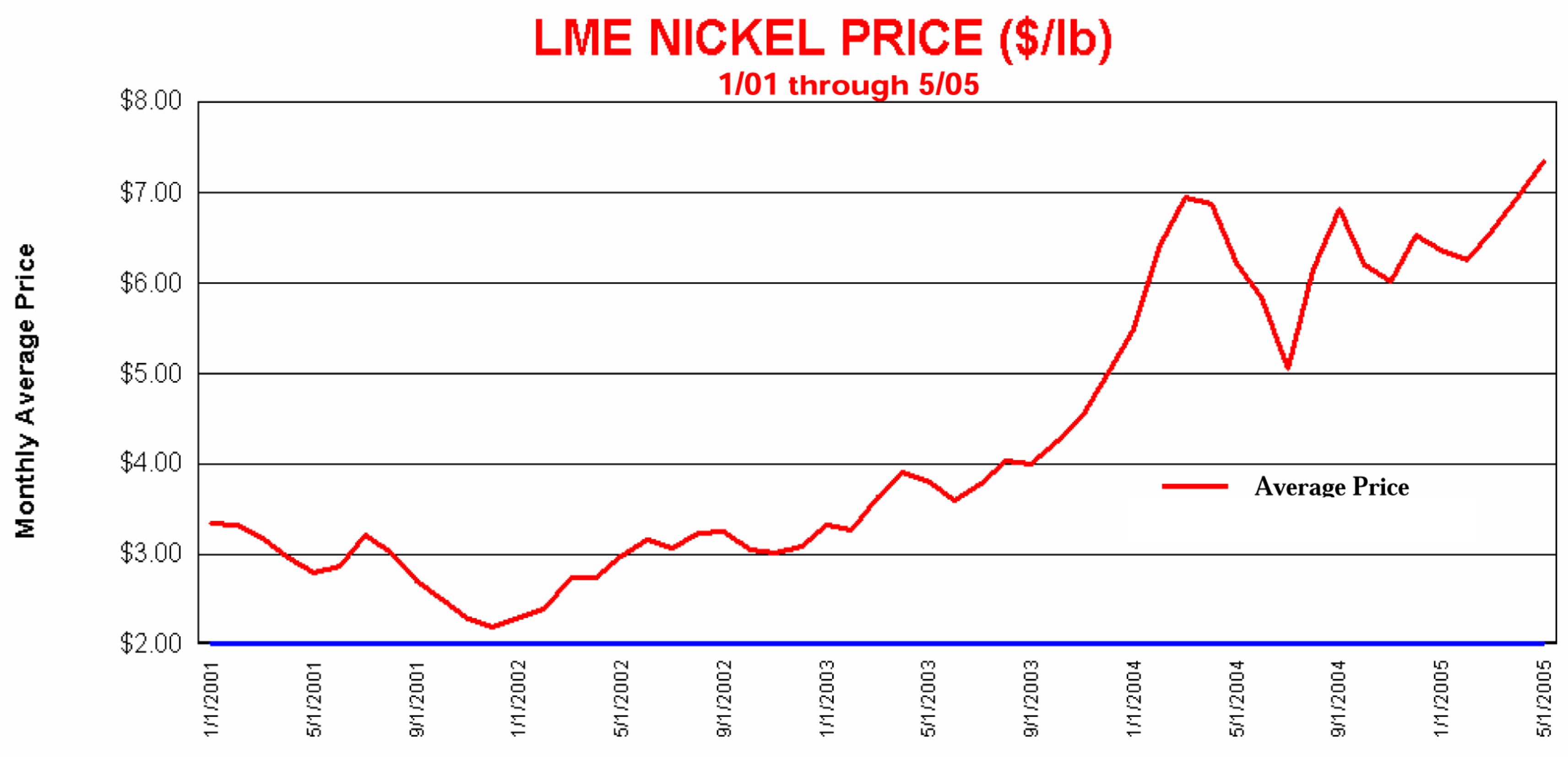
Optimal Production Process



Raw Material Challenges



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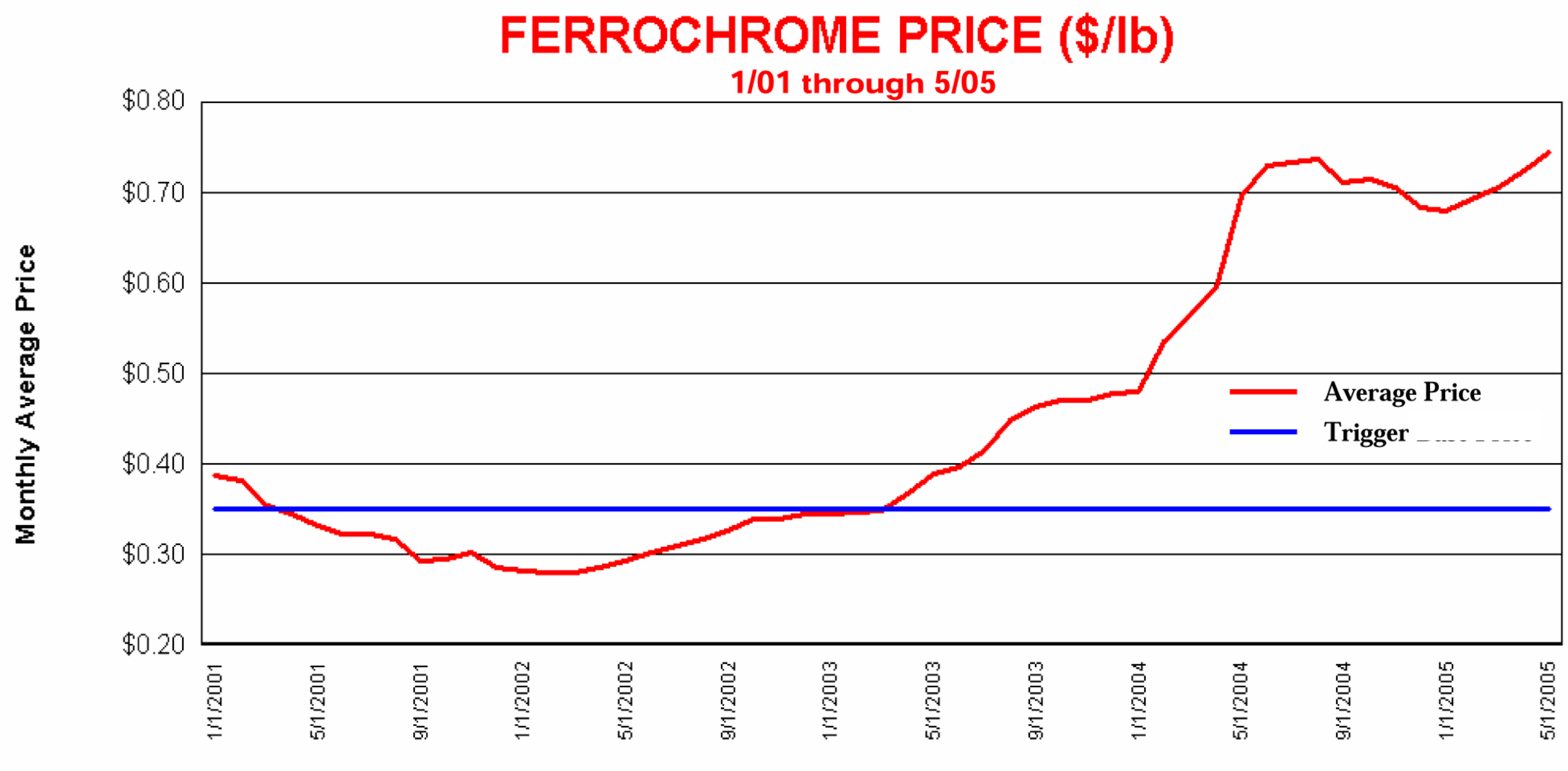
Raw Material Challenges



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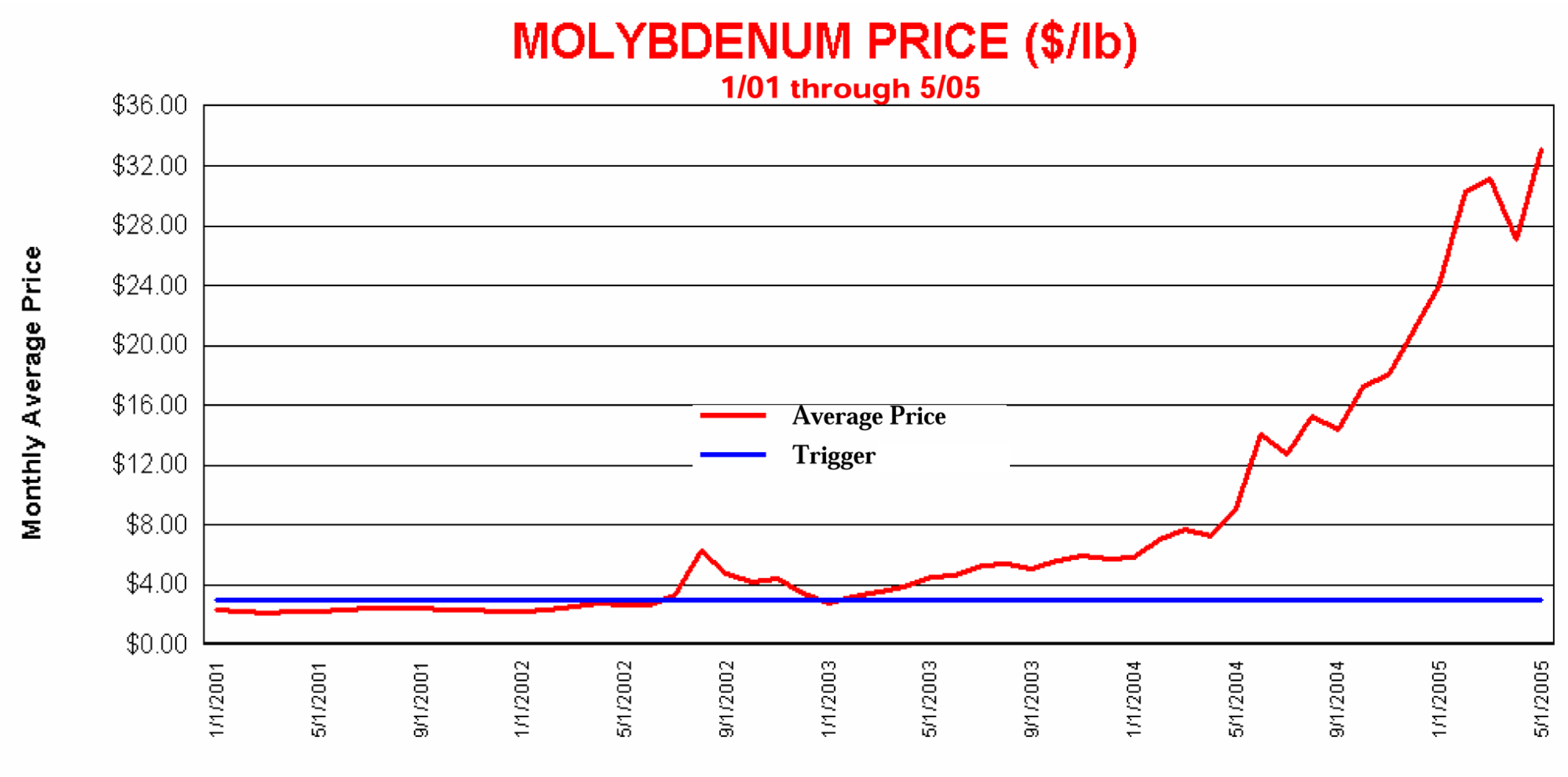

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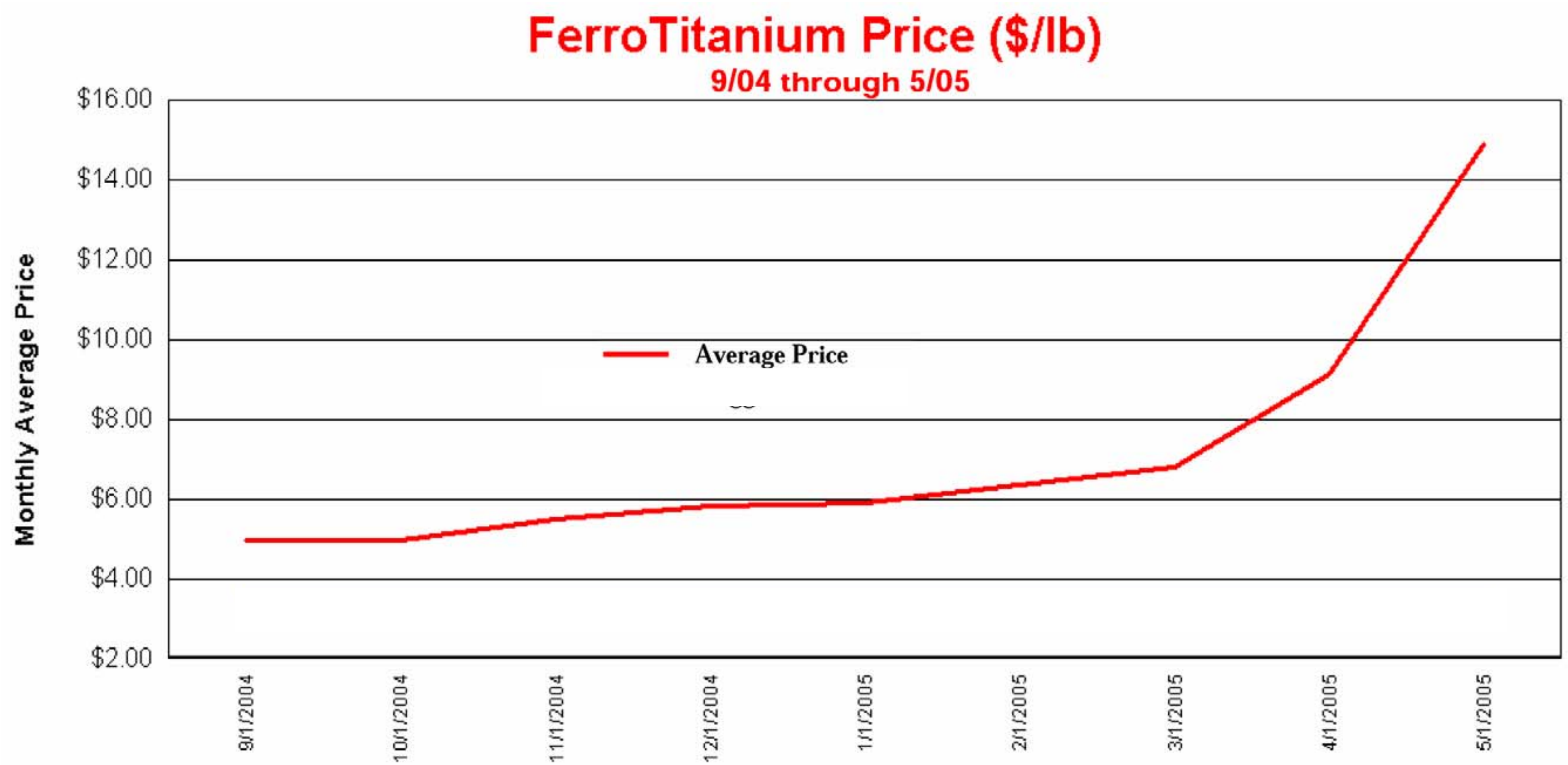
Raw Material Challenges



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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

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