Materials Processing Institute

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Disstec Workshop

Steel Cleanness Review

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Valorisation and Dissemination of Secondary Metallurgy Technology

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Steel Cleanness Review

"Steel is defined in terms of global composition, of distribution of phases, including the minor phases that are known as non-metallic inclusions, of microstructures and, more often than not, in terms of applications and properties in service."

Jean-Pierre Birat, 'Steel Cleanliness and Environmental Metallurgy', Conference on Clean Steels, 8-10 September, 2015, Budapest, Hungary

Steel Cleanness Review

Contents

- Clean steel requirements for steel grade and application
- Direct and indirect methods for evaluating steel cleanness
- Operational practices to improve steel cleanness at the ladle, tundish, and caster

Steel Cleanliness Requirements for Various Steel Grades

- Steel cleanliness depends on the amount, morphology and size distribution of non-metallic inclusions in steel
- The definition of "Clean Steel" varies with steel grade and its end-use

Steel product	Maximum impurity fraction	Maximum inclusion size
IF steel Automotive & deep-drawing Sheet	[C]≤30ppm, [N]≤40ppm, T.O≤40ppm [7], [C]≤10ppm[8], [N]≤50ppm[9] C]≤30ppm, [N]≤30ppm [10]	 100μm [10, 11]
Drawn and Ironed cans	[C]≤30ppm, [N]≤30ppm, T.O≤20ppm [10]	20μm[10]
Alloy steel for Pressure vessels	[P]≤70ppm[12]	
Alloy steel bars	[H]≤2ppm, [N]≤10-20ppm, T.O≤10ppm [13]	
HIC resistant steel (sour gas tubes)	[P]≤50ppm, [S]≤10ppm[12, 14]	
Line pipe	[S]≤30ppm [12], [N]≤35ppm, T.O≤30ppm [13], [N]≤50ppm[9]	100μm[10]
Sheet for continuous annealing	[N]≤20ppm[12]	
Plate for welding	[H]≤1.5ppm[12]	
Bearings	T.O≤10ppm[12, 15]	15μm[13, 15]
Tire cord	[H]≤2ppm, [N]≤40ppm, T.O≤15ppm[13]	10μm[13]
Non-grain-orientated Magnetic Sheet	[N]≤30ppm [9]	
Heavy plate steel	[H]≤2ppm, [N]30-40ppm, T.O≤20ppm[13]	Single inclusion 13μm[10] Cluster 200μm[10]
Wire	[N]≤60ppm, T.O≤30ppm[13]	20μm[13]

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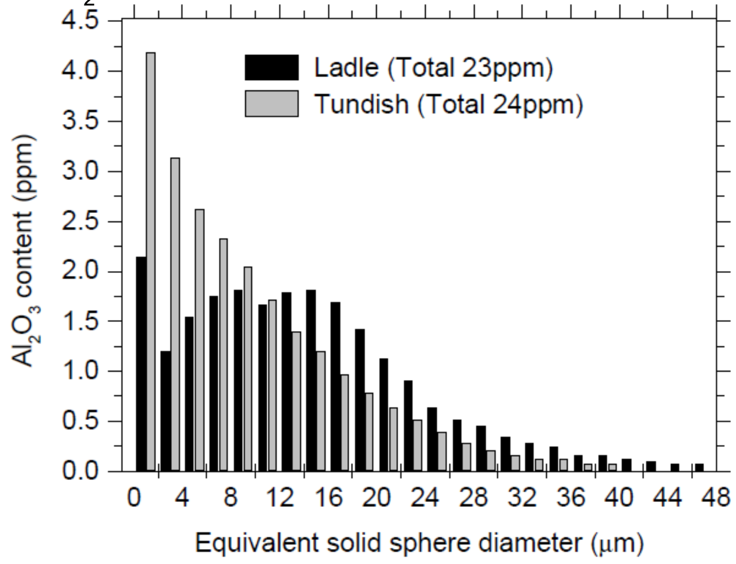
Influence of Common Steel Impurities on Steel Mechanical Properties

Element	Form	Mechanical properties affected
S,O	Sulfide and oxide inclusions	• Ductility, Charpy impact value, anisotropy • Formability (elongation, reduction of area and bendability) • Cold forgeability, drawability • Low temperature toughness • Fatigue strength
C,N	Solid solution	• Solid solubility (enhanced), hardenability
	Settled dislocation	• Strain aging (enhanced), ductility and toughness (lowered)
	Pearlite and cementite	• Dispersion (enhanced), ductility and toughness (lowered)
	Carbide and nitride precipitates	• Precipitation, grain refining (enhanced), toughness (enhanced) • Embrittlement by intergranular precipitation
P	Solid solution	• Solid solubility (enhanced), hardenability (enhanced) • Temper brittleness • Separation, secondary work embrittlement

Inclusion Size Distribution

- Large macro-inclusions are the most harmful to mechanical properties
- Detecting rare large inclusions is very difficult
- Large inclusions are far outnumbered by small ones but their total volume fraction may be larger
- Sometimes a catastrophic defect is caused by just a single large inclusion in a whole steel heat
- Clean steel involves not only controlling the mean inclusion content but also avoiding inclusions larger than a critical size harmful to the product
- Tundish steel is 'cleaner' than steel in the ladle furnace despite having a slightly higher total oxygen content and more total inclusions

Al_2O3 inclusion size distribution in ladle and tundish



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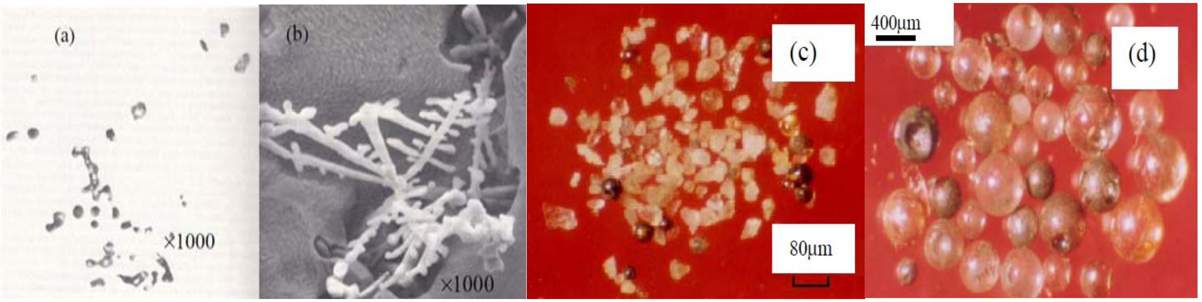
Typical Inclusions Morphology and Compositions

Non-metallic inclusions come from many sources, including:

- Deoxidation Products
  - Alumina inclusions form the majority of endogenous inclusions in LCAK steel
  - Generated by reaction between dissolved oxygen and added deoxidant, such as aluminium
  - Alumina inclusions are dendritic when formed in a high oxygen environment or may result from collision of smaller particles
- Reoxidation Products
  - Generated when dissolved aluminium in liquid steel is oxidised by FeO in the slag
  - Exposure to the atmosphere
- Slag Entrapment
  - Metallurgical fluxes are entrained during transfer between steelmaking vessels forming liquid inclusions that are usually spherical
- Exogenous Inclusions
  - Inclusions from other sources such as loose dirt, broken refractory or ceramic lining particles
  - Generally large and irregularly-shaped
- Chemical Reactions
  - For example from products of inclusion modification when Ca treatment is improperly performed



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Methods for Evaluating Steel Cleanliness

- Inclusion Amount/ Size Distribution/ Shape and Composition
  - Should be measured at all stages in steel production
  - NMI population depends on time (along process timeline) and on temperature
    - A ladle sample may give a good indication of cleanness at a point along the process timeline but this may have no correlation with cleanness in the solid steel
- Direct Methods
  - Accurate but costly
- Indirect Methods
  - Fast and inexpensive but only reliable as relative indicators

Methods for Evaluating Steel Cleanliness

Direct Methods

- Metallographical Microscope Observation (MMO)
  - 2-D method can give problems when interpreting slices through complex-shaped inclusions
- Image Analysis
  - Fast automated computer MMO evaluation can mistake scratches, pitting, and stains for NMI's
- Sulphur Print
  - Inexpensive 2-D method for detecting macro-inclusions
- Slime (Electrolysis)
  - Accurate but time consuming method to reveal individual, intact inclusions
- Electron Beam Melting (EB)
  - The EB index is the specific area of the formed inclusion raft
- Cold Crucible Melting (CC)
  - The method improves on Slime extraction by reducing the amount of metal to dissolve
- Scanning Electron Microscope (SEM)
  - Clearly reveals the 3-D morphology and composition of each NMI. Composition measured with Electron Probe Micro Analyser (EPMA)

Methods for Evaluating Steel Cleanliness

Direct Methods

- Optical Emission Spectroscopy with Pulse Discrimination Analysis (OES-PDA)
  - Dissolved elements in steel plus total oxygen content and micro-inclusion composition and size distribution
- Mannesmann Inclusion Detection by Analysis Surfboards (MIDAS)
  - Samples rolled to remove porosity and then ultrasonically scanned to detect solid macro-inclusions and compound solid macro-inclusions/ gas pores
- Laser-Diffraction Particle Size Analyser (LDPSA)
  - Evaluates the size distribution of inclusions extracted from steel sample using eg Slime method
- Conventional Ultrasonic Scanning (CUS)
  - Can obtain size distributions on NMI’s larger than 20µm in solidified steel samples
- Cone Sampling Scanning
  - A spiralling detector automatically detects surface inclusions in a cone shaped volume of a continuously cast product including from surface to centre-line
- Fractional Thermal Decomposition (FTD)
  - The total oxygen content is the sum of the oxygen contents measured at each heating step

Methods for Evaluating Steel Cleanliness

Direct Methods

- Laser Microprobe Mass Spectrometry (LAMMS)
  - Peaks in Lamms spectra are associated with elements based on comparison with reference sample results
- X-Ray Photoelectron Spectroscopy (XPS)
  - Uses X-Rays to map the chemical state of inclusions larger than 10μm
- Auger Electron Spectroscopy (AES)
  - Uses electron beams to map the chemical state of inclusions larger than sub-μm
- Photo Scattering Method
  - Photo-scattering signals of inclusions extracted by Slime, to give the size distribution
- Coulter Counter Analysis
  - Size distribution of inclusions extracted by Slime and suspended in water - similar to LIMCA
- Liquid Metal Cleanness Analyser (LIMCA)
  - Particles flowing into this on-line sensor through a small hole are detected as they change the electrical conductivity across the gap. Used for liquid aluminium rather than liquid steel
- Ultrasonic Techniques for Liquid System
  - Prototype on-line analyser - captures the reflections from ultrasound pulses to detect inclusions in liquid steel

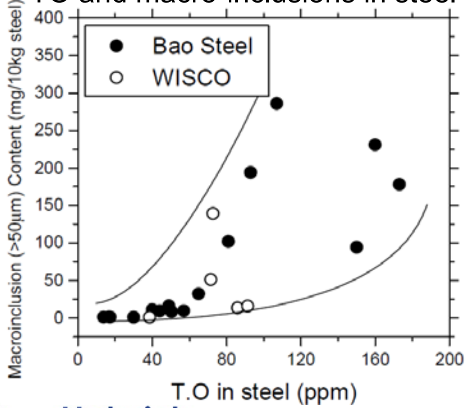
Methods for Evaluating Steel Cleanliness

Indirect Methods

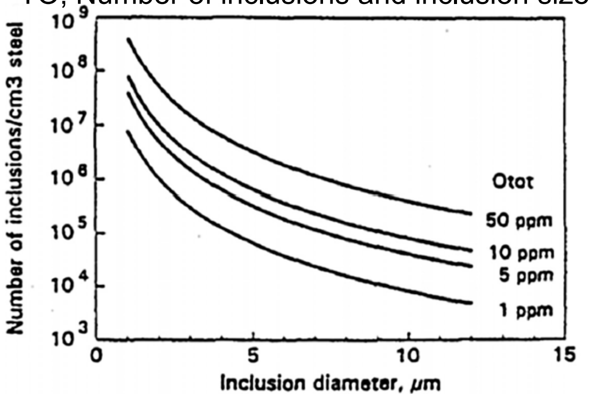
Because of cost, time constraints, and sampling difficulties, liquid steel cleanness is most often measured by using total oxygen, nitrogen pickup or other indirect methods

- Total Oxygen Measurement
  - Total Oxygen (TO) is the sum of dissolved (free) oxygen and oxygen combined as NMI's
    - ⇨ Dissolved oxygen is easily measured with an oxygen sensor
    - ⇨ For accurate TO measurement, TO samplers require argon protection and a fast cooling rate
    - ⇨ Process Route is important:- Ladle gas-stirring: TO ~ 35-45 ppm; RH-degassing: TO ~ 10-30ppm
    - ⇨ TO drops after every processing step - Ladle: 40ppm; Tundish: 25 ppm; Mould: 20 ppm; Slab: 15 ppm
    - ⇨ A low TO content generally represents the level of small oxide inclusions and decreases the probability of large oxide inclusions
    - ⇨ TO correlates strongly with the onset of Sliver defects. Heats are downgraded if tundish TO is too high

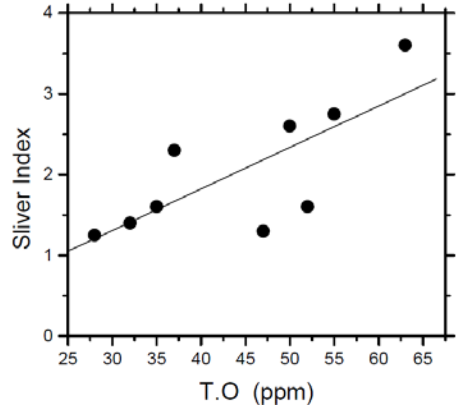
TO and macro-inclusions in steel



TO, Number of inclusions and inclusion size



TO in tundish and sliver defect index for product

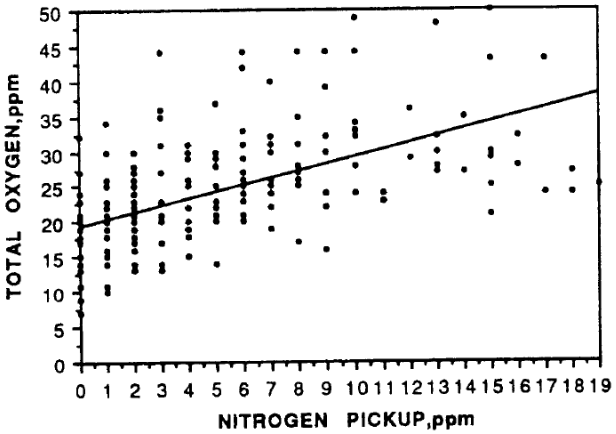


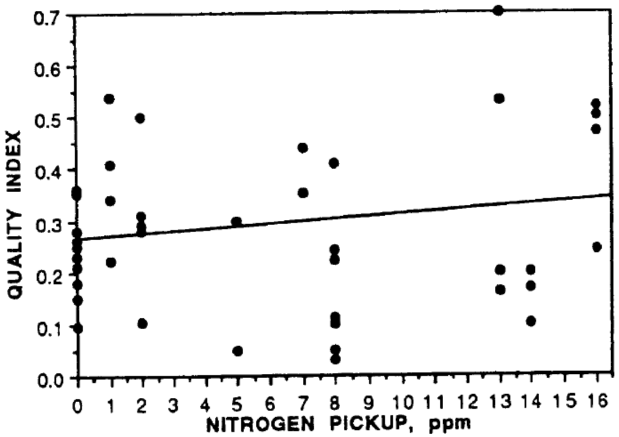
Methods for Evaluating Steel Cleanliness

Indirect Methods

- Nitrogen Pickup
  - Difference in nitrogen content between processing vessels (eg ladle to tundish or tundish to mould), is an indication of the amount of air entrained during transfer operations
  - It is a crude indirect measure of total oxygen, steel cleanliness and quality problems from reoxidation inclusions

Relationship between nitrogen pickup and total oxygen and steel quality index





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Methods for Evaluating Steel Cleanliness

Indirect Methods

- Dissolved Aluminium Loss Measurement
  - For LCAK steels, aluminium loss also indicates that reoxidation has occurred
  - This is less accurate than nitrogen pickup because Al can also be reoxidised by the slag
- Slag Composition Measurement
  - Change in slag composition before and after operations can indicate inclusion absorption
  - Slag entrainment from a previous vessel can be determined by tracking trace elements in the slag and inclusion composition
- Submerged Entry Nozzle (SEN) Clogging
  - Short SEN life due to clogging is often an indicator of poor steel cleanness

The above shows that there is no single ideal method to evaluate steel cleanness

Examples:

- ⇨ NSC used TO and EB melting for small inclusions and Slime and EB-EV for large inclusions
- ⇨ Baosteel used TO, MMO, XPS, and SEM for small inclusions; Slime and SEM for large inclusions; nitrogen pickup for reoxidation; slag composition analysis for inclusion adsorption and slag entrainment tracking

Operational Practices for Clean Steel

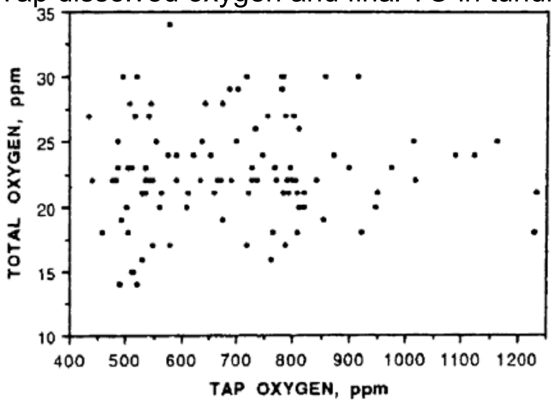
Ladle Operations

Ladle treatment lowers the inclusion population by 65%-75%; the tundish removes 20%-25%, although reoxidation sometimes occurs; the mould only removes 5%-10% - a relatively small effect

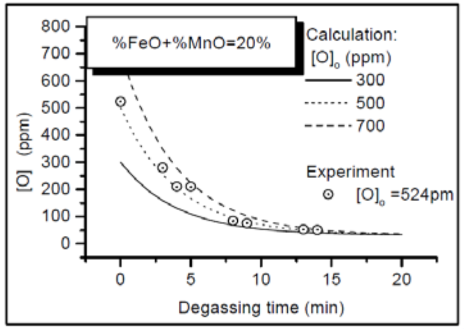
Tap Oxygen

- Tap oxygen content typically ranges from 250ppm to 1200ppm
- Aluminium additions can be added to deoxidise the steel which creates large amounts of Al_2O_3
- This implies that there should be a limitation on tap oxygen content for clean steel grades
- However, there is no correlation between tap oxygen and steel cleanness (TO)
- 85% of the alumina clusters formed after large aluminium additions readily float out to the ladle slag and the remaining clusters are smaller than ~30 μm
- The time available for floatation of Al_2O_3 clusters depends on the availability of ladle refining
- For example, degassing time must be adequate (eg ~15 min) to reduce TO to the same final value regardless of start level

Tap dissolved oxygen and final TO in tundish



Effect of tap oxygen ($[O]_o$) on TO removal in ladle during RH degassing



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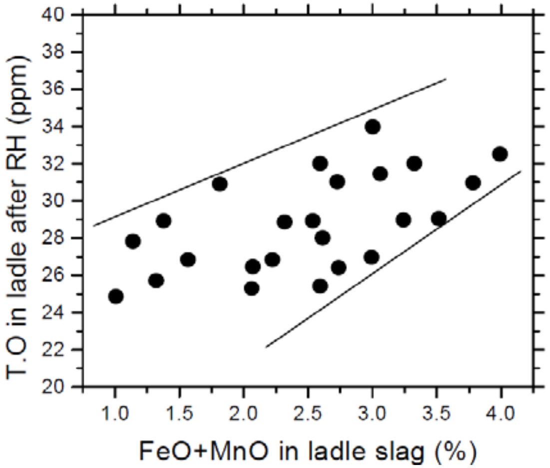
Operational Practices for Clean Steel

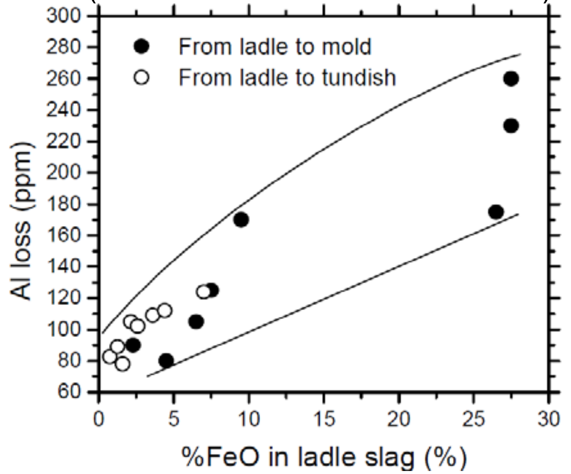
Ladle Operations

- FeO and MnO in the Slag
    - Carryover slag from converter or EAF contains large amounts of FeO and MnO
    - These oxides react with dissolved aluminium to generate alumina in liquid steel
    - TO in the ladle correlates with FeO+MnO in the ladle slag
    - Loss of dissolved Al correlates with FeO+MnO in the ladle slag

Relationship between FeO+MnO in ladle slag and TO



Effect of FeO+MnO in ladle slag on lowering dissolved Al (ladle to mould and ladle to tundish)



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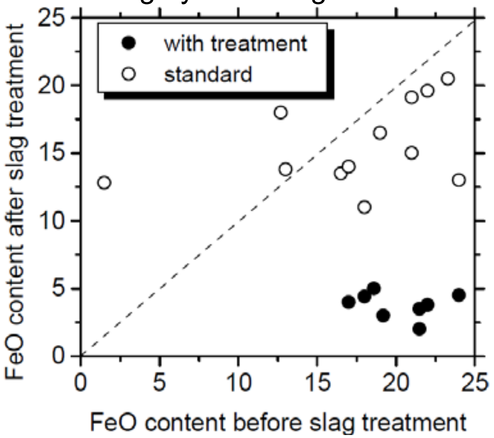
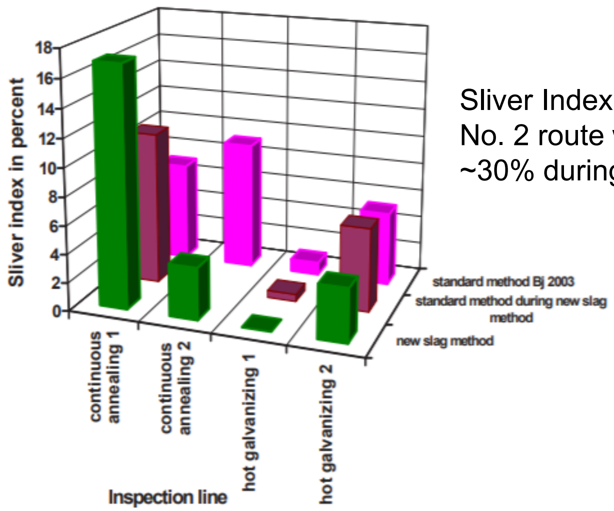
Operational Practices for Clean Steel

Ladle Operations

- Minimise Slag Carryover
  - Increase aim turndown carbon and avoid reblows to minimise dissolved oxygen content at tap
  - Use of sublance (in BOF) to reduce number of reblows
  - Use of slag stopper
  - Ladle skim to remove carryover slag from ladle top
- Ladle Slag Reduction
  - Minimise slag carryover + add basic ladle slag to reduce FeO%+MnO% to less than 1% to 2%
  - Add slag conditioner (mixture of aluminium and burnt lime or limestone) to lower FeO%+MnO%
    - FeO% +MnO% can be lowered to below 5%
    - Reports of significant improvements in coil cleanness
    - High cost procedure
    - Decision to implement is strategic

Reduction of FeO content in ladle slag by ladle slag reduction treatment





Sliver Index at hot galvanising No. 2 route was reduced by ~30% during a three month trial

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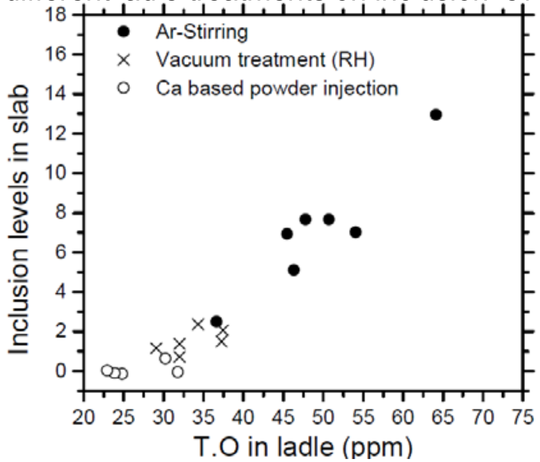
Operational Practices for Clean Steel

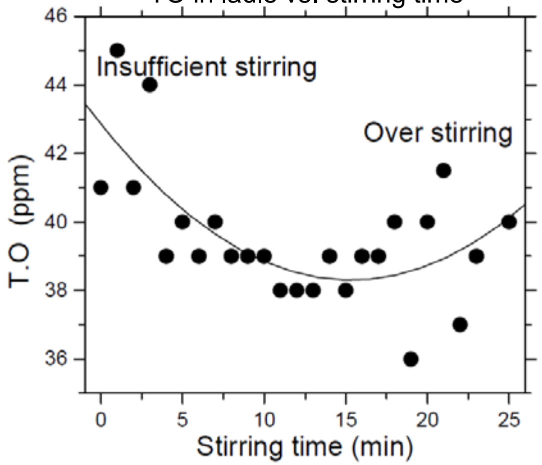
Ladle Operations

- Effect of Degassing and Ladle Stirring
  - Ladle stirring and refining processes such as vacuum treatment greatly promote inclusion agglomeration and removal
  - RH vacuum treatment improves steel cleanness to a greater extent than ladle stirring
  - Calcium-based powder injection treatment has a significant benefit in part due to high stirring power in addition to its capability for deoxidation and liquifying inclusions
  - Sufficient stirring time (>10 min) after alloy addition is required to allow alumina inclusions to circulate to the slag to be removed
  - Excessive stirring is detrimental – perhaps due to refractory erosion

Effect of different ladle treatments on inclusion level in slab



TO in ladle vs. stirring time



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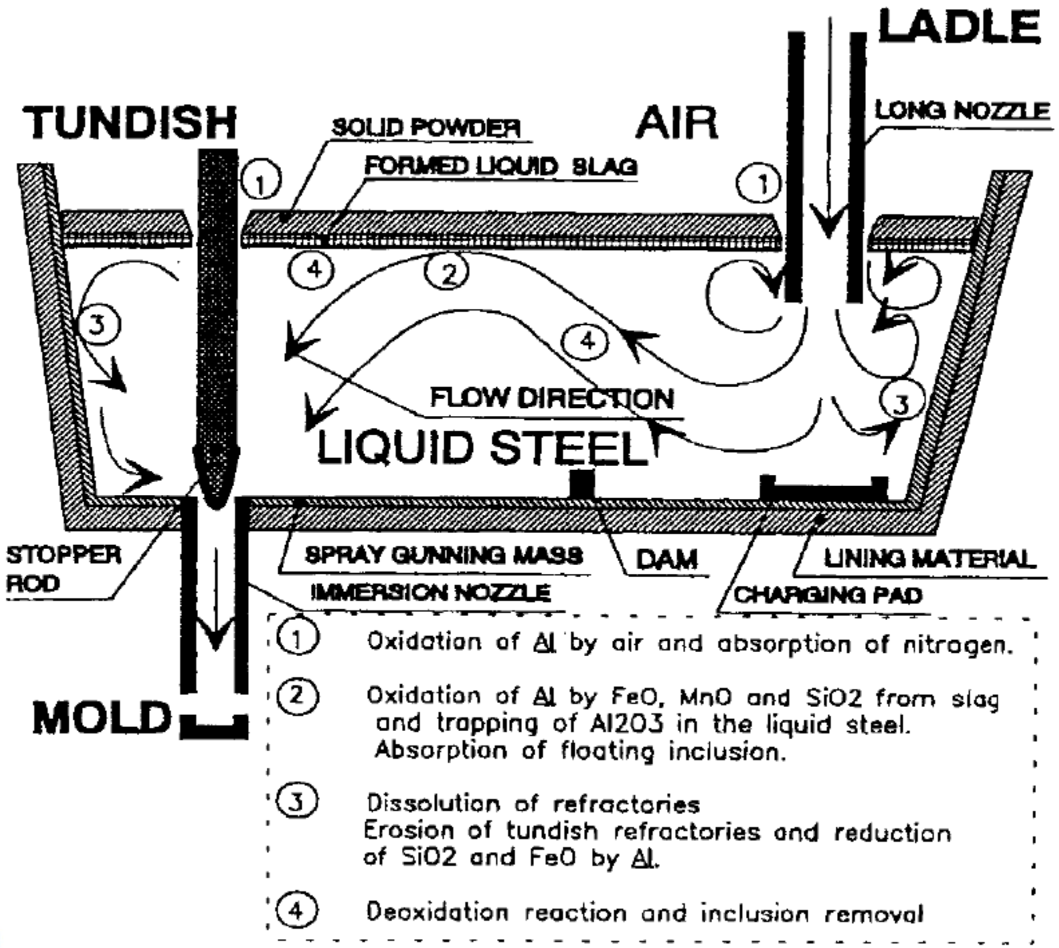
Operational Practices for Clean Steel

Tundish Operation

- Several important events take place in the tundish



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Operational Practices for Clean Steel

Tundish Operation

- Casting Transitions
  - These take place at the start of cast; during ladle change, ladle tube change, change of tundish, and SEN exchange; on speed changes; and at the end of a casting sequence
  - During these unsteady state casting periods, slag entrainment and air absorption are likely to take place which generates reoxidation issues
  - Inclusions are often generated during transitions and may persist for a long time thereby contaminating a lot of steel and best handled by downgrading part of the production
- Lining Refractory
  - Dissolved aluminium in the liquid steel reacts with any reducible oxide source in the lining refractory to promote reoxidation
- Tundish Flux
  - The tundish flux must provide several functions
    - Thermally insulate the molten steel bath to prevent excessive heat loss
    - Chemically insulate the molten steel bath to prevent air entrainment and reoxidation
    - Absorb inclusions to provide additional steel refining
    - Burnt rice husks are inexpensive; a good insulator; provide good coverage without crusting
    - Basic tundish flux has shown in some instances to reduce TO while in others it has shown no benefit; it develops a surface crust owing to the high melting rate and high crystallisation temperature; in general, it has low viscosity and therefore is more easily entrained into the steel bath

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Operational Practices for Clean Steel

Tundish Operation

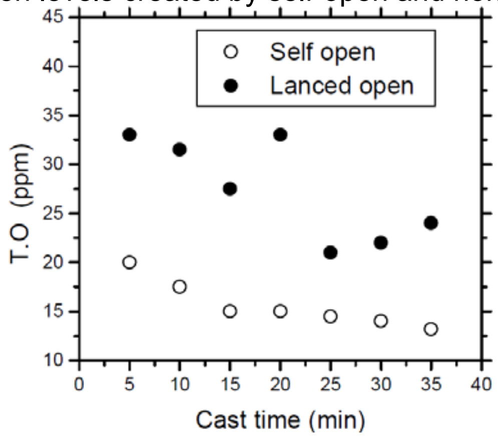
- Tundish Stirring
  - Injecting inert gas into the tundish from the bottom improves mixing of the liquid steel; promotes collision and removal of inclusions and has been shown to lower TO in the tundish
- Tundish Flow control
  - The tundish flow pattern should be designed to increase liquid steel residence time; prevent "short-circuiting"; and promote inclusions removal
  - Tundish flow is controlled by tundish geometry; its level; inlet (shroud) design; flow control devices such as impact pads, weirs, dams; baffles; and filters
  - The Turbostop impact pad has a proven record of improving steel cleanliness especially at start-up and ladle exchange by diffusing the momentum of the incoming steel stream
- Transfer Operations
  - Optimisation of the shrouding system is very important to prevent atmospheric reoxidation of steel during transfer from ladle to tundish or from tundish to mould
  - Reoxidation generates inclusions which cause production problems such as nozzle clogging and defects in the final product

Operational Practices for Clean Steel

Tundish Operation

- Ladle Opening
  - A self-opening ladle does not require oxygen lancing or prodding to open but opens on its own
  - For a non-self-opening ladle the shroud is first removed and the cast is left unshrouded from ladle to tundish so that reoxidation by air occurs for the first ⅔m to 1.3m of the cast
  - Non-self-open casts have TO levels ~10ppm higher than self-open casts
- Argon Protection
  - Argon protection is used to prevent liquid steel from air reoxidation
  - This can involve purging the tundish with argon just prior to to ladle opening and by incorporating appropriate gas injection into the shrouding system
- Sealing Issues
  - Close attention must be paid to appropriate design and maintenance of the shroud seals between ladle and tundish and the SEN from tundish to mould

Total oxygen levels created by self-open and non-self-open casts



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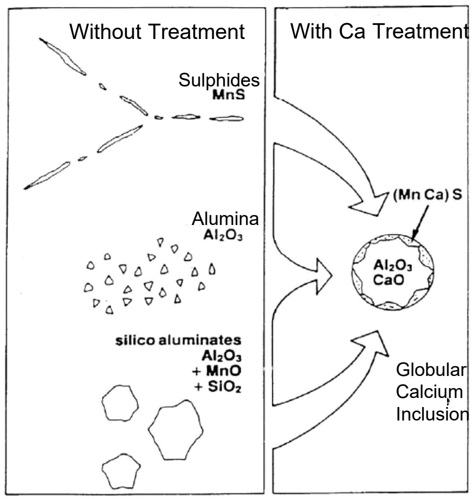
Operational Practices for Clean Steel

Tundish Operation

- Nozzle Clogging
  - Disslodged Clogs either become trapped in the steel or they can change the flux composition leading to defects in either case
  - Clogs change the nozzle flow pattern and jet characteristics exiting the nozzle which disrupts flow in the mould leading to slag entrainment and surface defects
  - Clogging interferes with mould level control as it tries to compensate for the clog
- Calcium Treatment
  - Inclusions are modified in the ladle with Calcium powder or wire injection
  - Calcium Aluminates, with a composition close to the eutectic, are liquid and therefore globular at steelmaking temperature
  - Therefore, there is no deposit and no clogging



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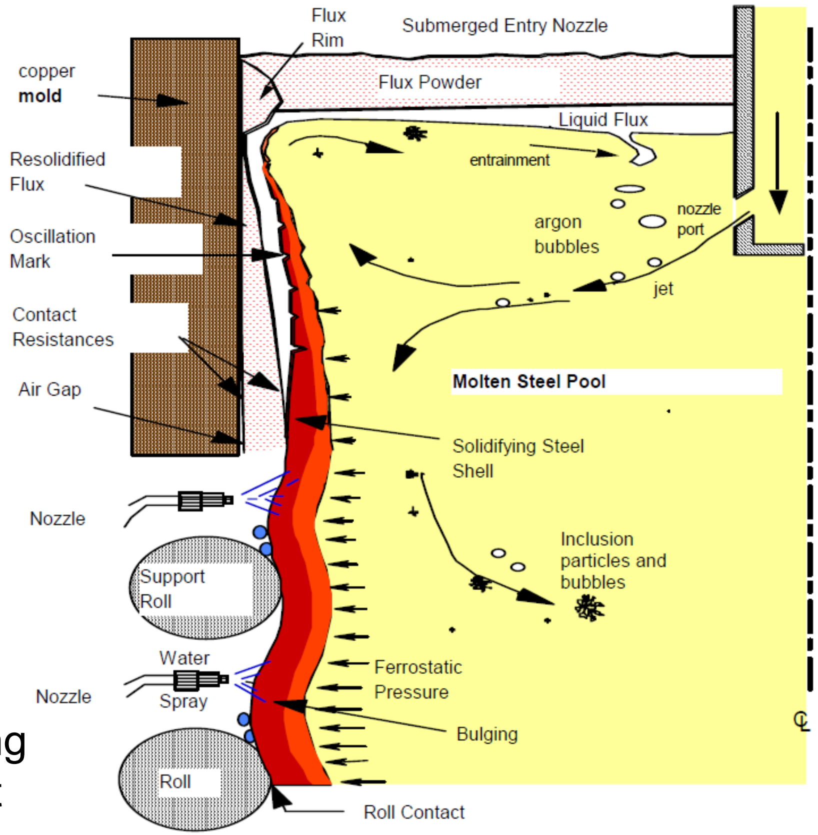
Operational Practices for Clean Steel

Mould and Caster Operation

Inclusions in the Mould

- NMI's carried over into the concast mould can cause various kinds of defects during continuous casting, including breakouts or major surface defects
- Inclusions may derive from deoxidation products; nozzle clogs; entrained tundish/ ladle slag; and reoxidation products from air absorption and nozzle leaks
- Mould slag may be entrained by excessive top surface velocities or surface fluctuations
- New inclusions may precipitate as the superheat drops
- They can be safely removed into the slag/ steel interface by buoyancy flotation, fluid flow transport and attachment to bubbles
- They can become entrapped into the solidifying shell to form permanent defects in the product

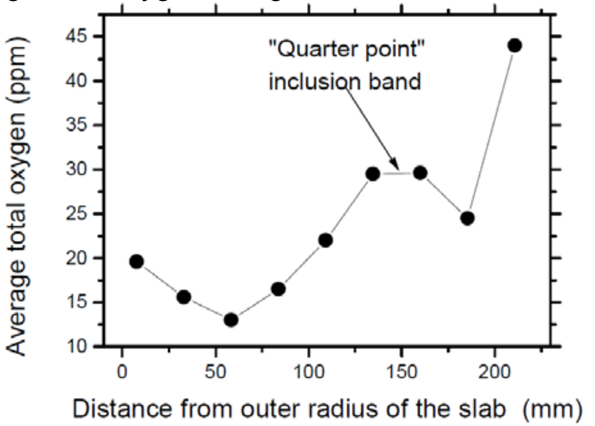


Operational Practices for Clean Steel

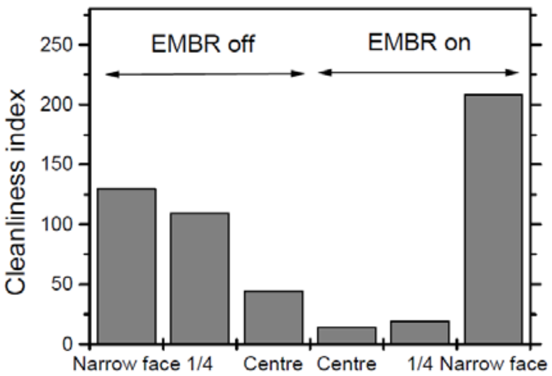
Mould and Caster Operation

- Inclusions in the Mould
  - Curved mould machines entrap more inclusions than straight (vertical) mould casters
  - In curved mould machines inclusions are preferentially trapped 1-3m below the meniscus
  - Inclusions concentrate one-eighth to one-quarter of the thickness from the top inside radius surface
- Cast Speed
  - High casting speed and high variation in cast speed results in a higher rate of slivers
- Electromagnetic Brake (EMBR)
  - EMBR bends the jet and shortens its impingement length, moving inclusions upwards towards the mould powder or solidified shell at the slab surface

Average total oxygen along the thickness of the slab



Effect of EMBR on steel cleanness



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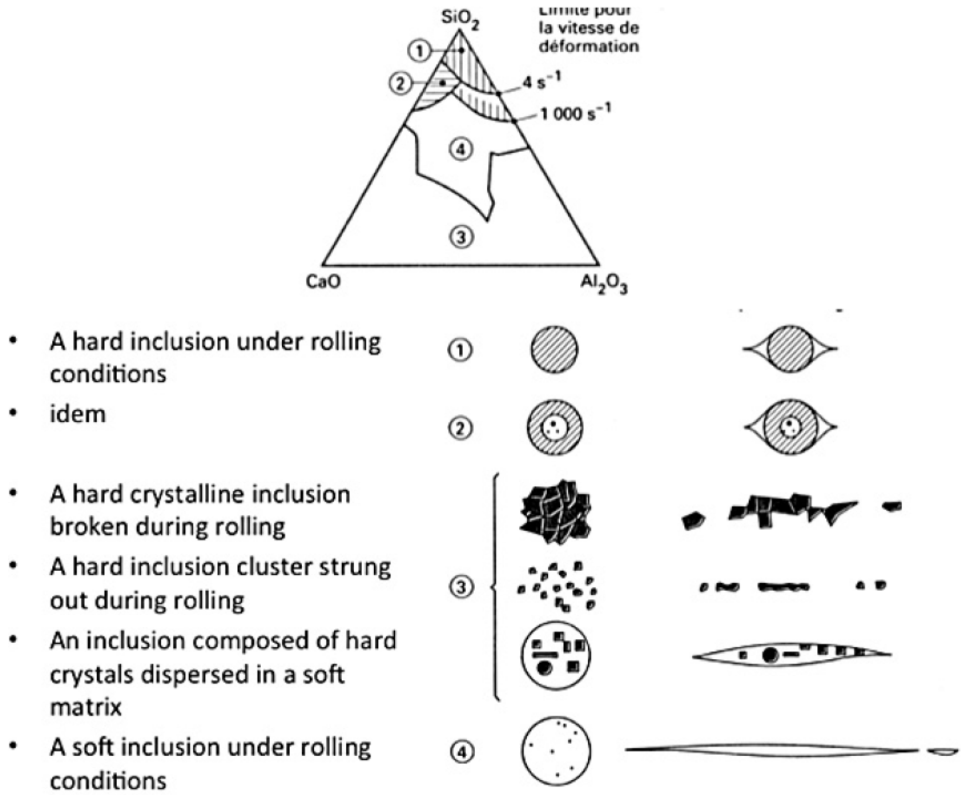
Operational Practices for Clean Steel

Mould and Caster Operation

Inclusions in the Solid Product

- Many NMI's are trapped in the metal at solidification
- NMI's will deform during hot rolling either compatibly or differently
- This leads to weaknesses: separations and internal cracks; traps for hydrogen; and anisotropy between longitudinal and transverse directions
- At the surface they can cause superficial defects which can be un-aesthetic or initiate cracks or corrosion
- In tough high strength steels, they can behave as internal cracks, even with matrix continuity and influence fatigue properties in a detrimental way by significantly lowering the fatigue limit of steel
- Very high-end applications resort to remelting under vacuum after the step of very clean production of the remelting electrode



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