Calcium modification of alumina and spinel inclusions in aluminum-killed steel

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Topics considered

✧ Transient reaction products upon Ca treatment: CaS & CaO
✧ Modification of spinel (MgO.Al₂O₃) inclusions
✧ Size & matrix effects on SEM/EDX inclusion analysis
Solid Oxide Inclusions in Al-killed steel

**Alumina**

From Al deoxidation

\[ 2[\text{Al}] + 3[\text{O}] \rightarrow \text{Al}_2\text{O}_3 (s) \]

**Spinel**

- \( \text{MgAl}_2\text{O}_4-\text{Al}_2\text{O}_3 \) solid solution
- Mg source: mainly ladle slag

Clustered alumina inclusion

**Solid inclusions tend to clog submerged-entry nozzle (etc.) in continuous caster**
Tundish nozzle plug
(Al-killed steel)

Why calcium treat?

Liquidus temperatures of Al₂O₃-CaO (-MgO) mixtures

CaO:
- more stable than Al₂O₃
- lowers liquidus temperature

MgO:
- contributes to liquefaction

FactSage

Graph showing liquidus temperature as a function of CaO/(CaO+Al₂O₃) mass ratio with two curves: No MgO and 5% MgO, and a dashed line indicating the casting temperature.
Possible reactions upon injection of Ca into liquid steel

Injected Ca

Dissolution

+[S]

+[O]

+[Al\textsubscript{2}O\textsubscript{3}]

+[MgAl\textsubscript{2}O\textsubscript{4}]

[Ca]

<CaS>

<CaO>

Ca aluminate

Majority: evaporates

?
Extent of Ca dissolution in steel: unknown

Proposed Ca-O-<CaO> relationships in liquid steel (JSPS, 2010)
Extent of Ca dissolution in steel: unknown

Proposed Ca-O-<CaO> relationships in liquid steel (JSPS, 2010)
Current best guess:
Dissolved calcium in Ca-treated steel: ~ppm
Total calcium content: ~20 ppm

⇒ Most calcium present as reaction products. What are these?
- studied by sampling steel immediately after Ca treatment
- laboratory and industrial samples
- steel samples examined by SEM/EDX
  ✦ automated analysis of polished sections
  ✦ manual SEM:
    • inclusions in polished sections
    • inclusions extracted by dissolving steel matrix
Experimental Procedure

Power Supply
Pyrometer
Vacuum System
MgO crucible
Ar cylinder

SAMPLING TOOL
Off Gas
Sampling tube
CaSi₂
Al/Al-Mg

VACUUM INDUCTION FURNACE
Evacuation + Ar backfilling
Melting of Iron
Deoxidation of Steel (Al-Mg alloy)
Calcium Treatment (CaSi₂)
Inclusion detection and analysis using polished cross-sections

Backscattered electron image: inclusions dark; steel bright

Detected inclusions

Quantified composition

Analyzed X-ray spectrum

Hundreds of inclusions analyzed in tens of minutes
Displaying results: proportional symbol plot

Area of triangle in the modified plot is proportional to number of inclusions (similar to a "bubble plot")
"Bubble chart" example

(bubble size $\propto$ annual CO$_2$ emissions)

Previously proposed initial reactions upon Ca injection

Lu, Irons & Lu: "A kinetic study of calcium wire injection into steel"
First International Calcium Treatment Symposium, 1988
This work: initial formation of CaS / CaO confirmed; CaS and CaO react further to modify Al$_2$O$_3$.

These images: inclusions extracted / exposed by dissolving steel matrix in bromine-methanol.
This work: initial formation of CaS / CaO confirmed

INCA Feature analysis, 10 kV

Industrial sample: Ladle (immediately after Ca treatment)

Proportional symbol map: distribution of inclusion compositions found in polished sections
This work: initial formation of CaS / CaO confirmed

INCA Feature analysis, 10 kV

Proportional symbol map:
distribution of inclusion compositions found in polished sections

Industrial sample: Caster mold
(long after Ca treatment)
Expected inclusion composition changes:

\[ 3\langle \text{CaS} \rangle + \langle \text{Al}_2\text{O}_3 \rangle \rightarrow 3(\text{CaO}) + 2[\text{Al}] + 3[\text{S}] \]
Modification of spinel inclusions

- Composition: MgAl$_2$O$_4$-Al$_2$O$_3$ solid solution
- Formation: reduction of MgO from slag
- Cause clogging, like alumina
- If Ca modified, MgO contributes to liquefaction

Spinel cluster
(extracted with bromine-methanol)
Spinel inclusions in deoxidized steel

Proportional symbol map:
distribution of inclusion compositions found in polished sections
Ca treatment partially removes MgO from inclusions

Proportional symbol map: distribution of inclusion compositions found in polished sections
Modification of spinels: initial formation of CaS; MgO removed from spinel during Ca treatment

These images: inclusions extracted / exposed by dissolving steel matrix in bromine-methanol
Modification of spinel inclusions

- Readily modified to liquid / partially liquid inclusions
- Partial removal of MgO (Mg enters liquid steel) upon calcium treatment
- Similar transient path to alumina (CaS forms first, then reacts to give modification)
- [Mg] returned to solution upon Ca treatment: spinels can reappear upon reoxidation
Analysis of micron-sized inclusions: sources of inaccuracy

- Not all inclusions detected
  (<1 µm inclusions not analyzed)
- Matrix distorts analysis
Significant proportion of inclusions is not detected by SEM/EDX.

Comparison of total O and Ca of steel, with O and Ca contained in detected inclusions.

Sample: 2 min after Ca.
Size distribution of detected inclusions (cross-sections) (only inclusions $\geq 1 \, \mu m$ analyzed)
Matrix effect:

X-rays pass through inclusion and steel matrix

Interaction volume
Matrix effect:
Steel matrix filters Al & Mg X-rays
Matrix effect:
Analyzed Ca content too high; varies with size & kV

DTSA-II simulations
Matrix effect:
Depends on kV (size of interaction volume)

Interaction volumes

Material: Ca$_4$Al$_4$MgO$_{11}$

CASINO simulations
Predicted matrix effect confirmed by simulation and measurements

Inclusion geometries considered:

a) Cube
b) Truncated sphere
c) Hemisphere
d) Spherical cap
Line scan across inclusion in two directions

![Diagram showing a circle with points (0, r_{app}), (-r_{app}, 0), (0, -r_{app}), (r_{app}, 0)]

towards detector
Line scans across inclusions: predicted effect

PENEPMA simulations
Line scans across inclusions: measured effect
Acceleration voltage: predicted effect

**PENEPEMA simulations**

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**Graph a:**
- Cubes
- Inclusion width (μm)
- Relative error in Ca/Al ratio

**Graph b:**
- Truncated spheres
- Apparent diameter (μm)
- Relative error in Ca/Al ratio
- Curve markers:
  - 10kV
  - 15kV
  - 20 kV
Acceleration voltage: measured effect

![Graphs showing the effect of acceleration voltage on calcium to aluminum ratio.](image)
Conclusions

- Transient reaction products form upon Ca treatment: CaS & CaO
- CaS & CaO react further with alumina & spinel to yield modified inclusions (calcium aluminates)
- Spinel (MgO.Al$_2$O$_3$) inclusions modified readily; MgO partially removed from inclusions upon Ca treatment
- Analyses affect by:
  - matrix
  - non-analysis of <1 µm inclusions