Solidification under continuous casting conditions, thermodynamic and experimental studies

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CALPHAD & steelmaking

- **Carbon equivalent formulae**
  \[ C_p = [%C] + X_{\text{Mn}}[%\text{Mn}] + X_{\text{Si}}[%\text{Si}] + \ldots \]
The solidification of a steel will be a fingerprint that marks many properties of the final product.

Example 2: Segregation and banding
Ennis et al., Acta Mater., 115, 132-142. 10.1016/j.actamat.2016.05.046
As-cast dendritic structure
Elemental line profiles of martensite/austenite bands embedded in the ferrite matrix in CRA, showing inverse segregation of Al and Mn.
Origin of ferrite streaks

DSP FV85 dendritic structure

"stretched" as-cast slab

‘Zorro’ lines/ ferrite streaks (and centre-line segregation) in a HR strip
Ferrite streaks correlated to Mn depletion of primary dendrite formation
### Relationship cast structure and banding

![Image](image-url)

<table>
<thead>
<tr>
<th>Process step</th>
<th>As cast Production</th>
<th>Hot rolled Production</th>
<th>Cold-rolled and annealed Laboratory* Production</th>
<th>Cold-rolled and annealed Laboratory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample thickness, mm</td>
<td>225</td>
<td>3.0</td>
<td>3.4</td>
<td>1.0</td>
</tr>
<tr>
<td>Rolling reduction, %</td>
<td>n/a</td>
<td>99</td>
<td>95</td>
<td>66</td>
</tr>
<tr>
<td>Predicted dendrite arm spacing, µm</td>
<td>370-400</td>
<td>5.0 ±0.2</td>
<td>17.2 ±1.5</td>
<td>1.7 ±0.1</td>
</tr>
<tr>
<td>Measured distance between segregation and second phase bands, µm</td>
<td>380 ±36</td>
<td>no data</td>
<td>12.1 ±4</td>
<td>1.9 ±0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6.2 ±0.8</td>
</tr>
</tbody>
</table>

* As-cast thickness of samples hot- and cold-rolled in the laboratory was 75mm

Elemental line profiles of martensite/austenite bands embedded in the ferrite matrix in the studied steel after cold-rolling and annealing (CRA), showing inverse segregation of aluminium and manganese.
Homogenisation during reheating: fact vs. fiction

- Single component diffusion of Al in Fe indicates homogenisation times from seconds to hundreds of hours at 1250°C

<table>
<thead>
<tr>
<th>Base material</th>
<th>Aluminium composition range, wt.%</th>
<th>Temperature range, °C</th>
<th>$D_0$, $10^{-12}$ m$^2$s$^{-1}$</th>
<th>$Q$, kJmol$^{-1}$</th>
<th>Homogenisation time at 1250°C, s</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>bcc-Fe</td>
<td>not reported</td>
<td>897 – 1097</td>
<td>5.15</td>
<td>245.8</td>
<td>2561</td>
<td>[46]</td>
</tr>
<tr>
<td>bcc-Fe</td>
<td>0 – 5</td>
<td>920 – 1210</td>
<td>27.0</td>
<td>188</td>
<td>436</td>
<td>[47]$^\dagger$</td>
</tr>
<tr>
<td>fcc-Fe (AISI 316L)</td>
<td>not reported</td>
<td>500 – 640</td>
<td>5.0</td>
<td>184</td>
<td>170</td>
<td>[49]</td>
</tr>
<tr>
<td>ion implanted bcc-Fe</td>
<td>0 – 8</td>
<td>775 – 900</td>
<td>1.6</td>
<td>306</td>
<td>$1.1 \times 10^6$</td>
<td>[45]</td>
</tr>
<tr>
<td>0.15C-0.3Mn</td>
<td>0 – 34</td>
<td>950 – 1100</td>
<td>30.1</td>
<td>234.5</td>
<td>174</td>
<td>[44]</td>
</tr>
<tr>
<td>0.17C-0.5Mn-0.3Si steel (Q23S)</td>
<td>not reported</td>
<td>1020 – 1080</td>
<td>1.7</td>
<td>142</td>
<td>1.6</td>
<td>[48]</td>
</tr>
</tbody>
</table>

$^\dagger$ Incorrectly attributed to Tobin [50] in Smithells Metals Reference Book [47]; the latter reference will be used.
Homogenisation during reheating: fact vs. fiction

- DICTRA multi-component calculations:
  - diffusion of solid-state elements (Al/Mn) during reheating is too slow to result in chemical homogenisation
  - segregation profiles present after casting remain throughout the downstream processes

Distributions of C, Mn, Al along the diffusion path/boundary for time steps of 100, 1000 and 100,000 s (28 h)
The question is not *if* we can cast a steel, but *how* can we cast it…

Example 1: precipitation during continuous casting
AHSS

Example of the defect formation

Oscillation Mark  Bleeder  Cracking

End of solidification
\( T_s 1 = 1297^\circ C \) (steel with B)

End of solidification
\( T_s 2 = 1474^\circ C \) (steel without B)
Experimental methods

- Two methods have been adopted in the experimental work.

  Method A: Directional solidification and quenching (DSQ)

  Method B: Solidification and quenching (SQ)
The **directional transformation** of the alloy can be carried out from liquid to room temperature so that the consecutive liquid–solid and solid–solid transformation fronts in a given sample can be studied under well-defined steady-state conditions.\(^3\)

As fluid flow strongly influences the microstructures, its control and absence in **directional solidification** by the use of small diameter tubes is a powerful technique, complementary to space experiments.\(^3\)

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Withdrawal rate: 125 μm/s

Microstructure of directional solidification samples
Withdrawal rate: 25 μm/s

Microstructure of directional solidification samples
Withdrawal rate: 5 μm/s

Microstructure of directional solidification samples
For directional solidification, the structure along with the growth direction can be obtained at first. Then the sample can be cut to investigate the cross section.

Microstructure which is similar to the cross section can also be obtained by a method called solidification and quenching (SQ).

Schematic illustration of mushy zone that reveals nucleation and development of primary grains in different zones. [1]

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Method B; Solidification & quenching

Schematic diagram of the solidification and quenching process ranging from 1505 °C to 1415 °C at the interval of 10 °C.

Schematic diagram of the experimental equipment.
Method B; Solidification & quenching

Schematic diagram of measuring the temperature

The measured position is heart of the sample

The measured temperature history of the sample
Etched samples

Microstructures of the quenched samples which can indicate the solidification process.
Selected areas for EPMA

Microstructures of the studied surface on each sample.
Liquid & solid determination

Representative binary images of the microstructures.
Liquid & solid fraction

Experimental results compared with calculations.

<table>
<thead>
<tr>
<th>T</th>
<th>f_{m,s}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1475</td>
<td>58%</td>
</tr>
<tr>
<td>1465</td>
<td>76%</td>
</tr>
<tr>
<td>1455</td>
<td>88%</td>
</tr>
<tr>
<td>1445</td>
<td>92%</td>
</tr>
<tr>
<td>1435</td>
<td>96%</td>
</tr>
<tr>
<td>1425</td>
<td>97%</td>
</tr>
<tr>
<td>1415</td>
<td>100%</td>
</tr>
</tbody>
</table>

\[
\rho_L = 7.5 \times 10^{-4} (T_{L,start} - T) + 7.02 \quad (\times 10^3 \text{ kg} \cdot \text{m}^{-3})
\]

\[
\rho_s = \rho_L = 4.80 \times 10^{-4} (T_{\gamma,start} - T) + 7.41 \quad (\times 10^3 \text{ kg} \cdot \text{m}^{-3})
\]

\[
f_{s,V} = \frac{f_{m,s}}{\rho_s} + \frac{f_{m,L}}{\rho_L}
\]

T_{L,start} = 1505

T_{\gamma,start} = 1478
Conclusions

• Calphad method is very useful for the steel industry, many simple applications…

• The whole microstructure of the mushy zone can be obtained with directional solidification and S&Q methods, convenient to study the dendrite structure, element distribution, etc.

• Not really enough yet, but we are working on…..
Questions???

Persistence is to the character of man what carbon is to steel (Napoleon Hill), unless other elements are added to the composition...*

* Preposition No. 8, PhD thesis B. Santillana