HIGH TEMPERATURE PROCESSING SYMPOSIUM 2012
Swinburne University of Technology
6 – 7 February 2012, Melbourne, Australia

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Symposium Schedule

Day 1 (6 February 2012) in EN 313

8.30 to 9.00 Registration in 3rd Floor of Engineering (EN) Building
9.00 to 9.10 Welcome by Prof Linda Kristjanson (Vice-Chancellor Swinburne University of Technology)

Session 1 Chaired by: Dr M Akbar Rhamdhani (Swinburne)
9.10 to 9.40 01 – Keynote: Dr John Rankin (CSIRO PSE) - Energy Use in Metal Production
9.40 to 10.00 02 – Dr Nathan Webster (CSIRO/ANSTO) - Phase Formation in Iron Ore Sintering
10.00 to 10.20 03 – Prof Geoff Brooks (Swinburne) - New Approach to Nitrogen Control in EAF Steelmaking
10.20 to 10.40 04 – Dr Dianwei Zhang (University of Queensland) - Investigation and Application of Phase Equilibria in the System Al₂O₃-CaO-MgO-SiO₂ Relevant to BF Slag
10.40 to 10.55 Coffee/Tea in EN 204/205

Session 2 Chaired by: A/Prof Monaghan (University of Wollongong)
10.55 to 11.25 05 – Keynote: Prof Markus Reuter (Outotec) - Metals and Enabling Sustainability
11.25 to 11.45 06 – Dr Nawshad Haque (CSIRO) - Greenhouse Gas Emission Assessment of Bio-coke from Wood for Application as Bioanode in Aluminium Production
11.45 to 12.05 07 – Mr Saiful Islam (Swinburne) – Electrochemical Slag-Metal Reaction for Silicon Production
12.05 to 12.25 08 – Mr Thomas Eglinton (CSIRO Newcastle) – Integrating Solar Thermal Technology into the Australian Minerals Processing Industry
12.25 to 1.15 Lunch in EN 204/205 (Sponsored by Amira Int., CAST, CSIRO, Furnace Engineering, OneSteel)
### Session 3

Chaired by: Prof Geoffrey Brooks (Swinburne)

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<th>Topic</th>
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<tr>
<td>1.15 to 1.45</td>
<td><strong>Keynote: Prof Aibing Yu (UNSW) - Modelling and Simulation of Blast Furnace Ironmaking</strong></td>
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<tr>
<td>1.45 to 2.05</td>
<td>Prof Doug Swinbourne (RMIT University) - The Solubility of Gold in Metallurgical Slag</td>
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<td>2.05 to 2.25</td>
<td>Ms Yan Li (UNSW) - Behavior of Impurities in Chlorination of Reduced Murray Basin Ilmenite</td>
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<td>2.25 to 2.45</td>
<td>Mr Stephen Bonner (University of Queensland-CAST) - Oxidation of Molten Aluminium</td>
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<tr>
<td>2.45 to 3.00</td>
<td>Coffee/Tea in EN 204/205</td>
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### Session 4

Chaired by: Mr Andrea Fontana (OneSteel)

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<tr>
<th>Time</th>
<th>Topic</th>
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<tr>
<td>3.00 to 3.30</td>
<td><strong>Keynote: Dr Ivan Ratchev (CSIRO PSE) - Process Modelling and Integration in Developing Sustainable Metals Extraction Technologies</strong></td>
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<td>3.30 to 3.50</td>
<td>Mrs Kun Mediaswanti (Swinburne) - Powder Metallurgy: A Promising Route for Bone Implants Fabrication</td>
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<td>3.50 to 4.10</td>
<td>A/Prof Xinmei Hou (University of Queensland-University of Science and Technology Beijing) – Functionalisation of Nitride Whiskers: Synthesis, Underlying Mechanism and Potential Applications as Membrane Filters</td>
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<td>4.10 to 5.00</td>
<td>Panel Discussion – <strong>What does the future hold for Australia's metallurgical industries?</strong> (led by Adjunct Prof John Grandfield) – Alan Clark, Wayne Stange, John Rankin, Ray Shaw, Mark Cooksey</td>
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**Close of Day 1**
Day 2 (7 February 2012) in EN 313

8.30 to 9.00  Registrations in 3rd Floor of Engineering (EN) Building

**Session 5**  Chaired by: Dr Mark Pownceby (CSIRO)

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<td>9.00 to 9.30</td>
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<td>Phase Equilibria Studies in the System “FeO”-SiO$_2$-CaO-Al$_2$O$_3$-MgO under Controlled Oxygen Partial Pressures</td>
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<td>9.30 to 9.50</td>
<td>Dr Peter Witt (CSIRO)</td>
<td>Use of CFD and Physical Experimentation to Understanding Slag Droplet Behaviour and Formation from a Spinning Disc</td>
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<td>9.50 to 10.10</td>
<td>Mr Othman Alzeghaibi (UNSW)</td>
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<td>10.10 to 10.30</td>
<td>Dr Mirco Wegener (CSIRO PSE)</td>
<td>Marangoni Instabilities in Single Droplet Extraction Systems</td>
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10.30 to 10.45  **Coffee/Tea in EN 204/205**

**Session 6**  Chaired by: Dr Marcus Zipper (CSIRO)

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<td>11.15 to 11.35</td>
<td>Dr Neslihan Dogan (University of Wollongong)</td>
<td>Why Do We Need New Inclusion Experimental Techniques?</td>
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<td>11.35 to 11.55</td>
<td>Dr Zheshi Jin (OneSteel Sydney Steel Mill)</td>
<td>Innovative Use of Rubber Tyres and Plastics in EAF Steelmaking</td>
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<td>11.55 to 12.15</td>
<td>Mr Morshed Alam (Swinburne)</td>
<td>CFD Modelling of Shrouded Jet Impingement on a Liquid Surface</td>
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12.15 to 1.15  **Lunch in EN 204/205 (Sponsored by Amira Int., CAST, CSIRO, Furnace Engineering, OneSteel)**

**Session 7**  Chaired by: A/Prof John Taylor (CAST CRC – U of Queensland)

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<tr>
<td>1.15 to 1.35</td>
<td>Dr Alex Deev (CSIRO)</td>
<td>Electrocapillary Phenomena in Molten Metal-Slag Systems</td>
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<td>1.35 to 1.55</td>
<td>Dr Luckman Muhmood (CSIRO)</td>
<td>Molten Slag Density Measurements with Focus on Slag Structures</td>
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<td>1.55 to 2.15</td>
<td>Mr Ata Fallah Mehrjardi (University of Queensland)</td>
<td>Effect of Bath Chemistry on the Heat Transfer Modelling of Freeze Lining in Copper Containing Slag System.</td>
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<td>2.15 to 2.35</td>
<td>Mrs Xijing Gloria Liu (University of Queensland)</td>
<td>Experimental Phase Equilibria study in Key Low Order Systems for Copper Smelting Slags</td>
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2.35 to 2.50  **Coffee/Tea in EN 204/205**
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<th>Session</th>
<th>Title</th>
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<td>3.10 to 3.30</td>
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<td>29 – Miss Jing Zhang (UNSW) - Gasification of Coke with CO₂</td>
</tr>
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<td>3.30 to 3.50</td>
<td></td>
<td>30 - Mr Mao Chen (University of Queensland) – Phase Equilibria and Preliminary Viscosity Studies of “Cu₂O”-SiO₂ –Al₂O₃ Systems in Equilibrium with Metallic Copper</td>
</tr>
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<td>3.50 to 4.10</td>
<td></td>
<td>31 – Mr Xing Xing (UNSW) - Micro-properties of Carbonaceous Materials</td>
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<td>4.10 to 4.15</td>
<td></td>
<td>32 – Mr Richard Simpson (Furnace Engineering) - CLOSING</td>
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**Close of Symposium**

4.15 to 5.00  Tour of the Robert Simpson High Temperature Laboratory at Advanced Technology Centre Building

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**Campus Map – Swinburne@Hawthorn**

[Campus Map Image]
Energy Use in Metal Production

John Rankin
CSIRO, Process Science and Engineering, Australia

Keywords: metals, embodied energy, primary metals, recycling, greenhouse

Energy is consumed at all stages in the production of primary metals – mining, beneficiation and chemical extraction – directly in the processes and indirectly through the production of inputs (such as electricity and reagents) used in the processes. The sum of the direct and indirect energies of the individual stages along the value-adding chain is the embodied energy of the metal. The embodied energy of the common metals varies widely, from typically around 20 MJ per kilogram for lead and steel to over 200 MJ per kilogram for aluminium (Figure 1.) The chemical transformation stages (leaching, smelting, electrowinning, etc) contribute the largest component and mining the least.

The main factors determining the embodied energy content of primary metals are:

- the stability of the minerals from which the metal is produced (determined by the ΔG of formation);
- the ore grade, since the lower the grade, the more ore that has to be mined and processed per unit of metal produced;
- the degree of beneficiation required, particularly grinding to achieve liberation since this is the most energy intensive operation in beneficiation; and
- the overall recovery, since losses along the value-adding chain require more ore to be mined per unit of metal produced.

Globally, of all the metals, steel production contributes the greatest quantity of greenhouse gases (Table 1), about 7% of global CO₂ produced from fossil fuels. This is because, although steel has a low embodied energy content it is produced in the largest quantity (about one billion tonnes per year). The annual production of aluminium is much lower than that of steel (about 38 million tonnes per year) but it is far more energy intensive and aluminium production is responsible for around 3% of global CO₂.

The quantity of greenhouse gases produced follows closely the trends in embodied energy (Table 1) though for those metals which require a high component of electrical energy, such as aluminium and magnesium, the source of electrical energy (coal, hydro, nuclear, etc) has a major impact on the quantities of greenhouse gases produced. For example, the embodied
energy in aluminium produced using electricity that is coal-based, natural gas-based and nuclear energy-based is approximately 22.4, 13.3 and 9.9 kg CO\textsubscript{2}-e/kg Al, respectively.

The energy required to recycle metals is a relatively small fraction of the energy required to produce metals from their ores since energy is required largely only for melting and not chemical transformation (Table 2). However, when the energy required for collection and separation of scrap is included, the embodied energy of recycled metals increases as the fraction of scrap collected increases since transportation and separation costs progressively increase.

Table 1: Global CO\textsubscript{2} production for primary production of metals (Note: electrical energy is assumed to be black coal based at 35\% efficiency).

<table>
<thead>
<tr>
<th>Metal</th>
<th>% of total metal production</th>
<th>Global annual production (Mt)</th>
<th>Embodied Energy (GJ per tonne)</th>
<th>Tonnes CO\textsubscript{2} per tonne metal</th>
<th>Global annual energy consumption (GJ)</th>
<th>Global annual CO\textsubscript{2} (tonnes)</th>
<th>% Global greenhouse gas production*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>pyro</td>
<td>80</td>
<td>15.6</td>
<td>33.0</td>
<td>3.25</td>
<td>6.1 x 10\textsuperscript{7}</td>
<td>6.0 x 10\textsuperscript{7}</td>
</tr>
<tr>
<td></td>
<td>hydro</td>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>pyro</td>
<td>60</td>
<td>1.66</td>
<td>113.5</td>
<td>11.45</td>
<td>2.4 x 10\textsuperscript{7}</td>
<td>2.2 x 10\textsuperscript{7}</td>
</tr>
<tr>
<td></td>
<td>hydro</td>
<td>40</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td>BF</td>
<td>89</td>
<td>3.55</td>
<td>19.6</td>
<td>2.07</td>
<td>7.5 x 10\textsuperscript{7}</td>
<td>7.8 x 10\textsuperscript{7}</td>
</tr>
<tr>
<td></td>
<td>ISP</td>
<td>11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc</td>
<td>electrolytic</td>
<td>90</td>
<td>10.5</td>
<td>48.4</td>
<td>4.61</td>
<td>4.9 x 10\textsuperscript{8}</td>
<td>4.7 x 10\textsuperscript{8}</td>
</tr>
<tr>
<td></td>
<td>ISP</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminium</td>
<td></td>
<td>100</td>
<td>38</td>
<td>211.5</td>
<td>21.81</td>
<td>8.0 x 10\textsuperscript{8}</td>
<td>8.3 x 10\textsuperscript{8}</td>
</tr>
<tr>
<td>Steel</td>
<td>BF/BOF</td>
<td>70</td>
<td>924</td>
<td>22.7</td>
<td>2.19</td>
<td>2.1 x 10\textsuperscript{6}</td>
<td>2.0 x 10\textsuperscript{6}</td>
</tr>
<tr>
<td>Cement</td>
<td></td>
<td>2 600</td>
<td>5.6</td>
<td>-0.9</td>
<td>1.46 x 10\textsuperscript{8}</td>
<td>2.3 x 10\textsuperscript{8}</td>
<td>8.1</td>
</tr>
</tbody>
</table>

*Global annual production of CO\textsubscript{2} from fossil fuel sources = 28 962 Mt (IEA, 2009)

Table 2: Energy for recycling metals after collection and sorting.

<table>
<thead>
<tr>
<th>Commodity</th>
<th>Embodied energy (GJ/tonne)</th>
<th>Embodied energy (as % of that of primary production)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Secondary Production*</td>
<td>Primary production</td>
</tr>
<tr>
<td>Plastic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paper</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminium</td>
<td>alloy</td>
<td>17.5</td>
</tr>
<tr>
<td></td>
<td>cans</td>
<td>18.1</td>
</tr>
<tr>
<td></td>
<td>no. 1 scrap</td>
<td>4.4</td>
</tr>
<tr>
<td></td>
<td>no. 2 scrap</td>
<td>20.1</td>
</tr>
<tr>
<td></td>
<td>low-grade scrap</td>
<td>49.3</td>
</tr>
<tr>
<td>Steel</td>
<td>billets</td>
<td>9.7</td>
</tr>
<tr>
<td>Lead – soft</td>
<td>batteries</td>
<td>9.4</td>
</tr>
<tr>
<td>Lead – hard</td>
<td>batteries</td>
<td>11.2</td>
</tr>
<tr>
<td>Nickel</td>
<td>alloy scrap</td>
<td>12.9</td>
</tr>
<tr>
<td>Zinc</td>
<td>new scrap slab</td>
<td>3.8</td>
</tr>
</tbody>
</table>

*Kusik and Kenahan (1978)

Technology plays an important role in reducing the embodied energy content of metals and greenhouse gas production and there has been progressive improvement over many decades. However, without step changes in technology, incremental improvements in energy efficiency become increasingly difficult to achieve. For example, the energy required for smelting aluminium in a modern smelter is around 13.5 kWh per kg Al which is about twice the theoretical amount required. However, this is approaching the limits of incremental
improvements to the Hall Heroult cell and further reductions in energy will require radically new technologies. Some examples of step change high temperature technologies include the top gas recycling blast furnace, heat recovery from slag, and thin strip casting.

However there is a limit to the energy reduction possible because of thermodynamic constraints, most importantly, the stability of the compound from which the metal is produced. There is a thermodynamic limit below which it is not possible to go. Present technology is far removed from that limit. For example, the theoretical limit for making steel from hematite is around 7 GJ per tonne Fe but modern iron and steelmaking practice requires around 20 GJ per tonne. Hence there remains much scope for further technical developments, particularly in removing energy intensive steps from existing processes, such as coke making and sinter making in steel production and carbon electrode production in aluminium production, or developing radically new processes with fewer steps and less materials handling; for example, the TIRO™ process for producing titanium (Doblin and Wellwood, 2008).

References

Phase Formation in Iron Ore Sintering

Nathan A.S. Webster$^{1,2}$, Mark I. Pownceby$^1$ and Ian C. Madsen$^1$
$^1$CSIRO Process Science and Engineering, Box 312, Clayton South, VIC, 3169, Australia
$^2$The Bragg Institute, ANSTO, Locked Bag 2001, Kirrawee DC, NSW, 2232, Australia

**Keywords:** Iron ore sintering, SFCA phases, Phase formation, In situ synchrotron XRD.

During the iron ore sintering process, iron ore fines (< 6 mm) are mixed with limestone flux and coke breeze and heated to ~1300°C. This results in partial melting of the mixture, and converts the loose raw materials into a porous but physically strong composite material in which the iron bearing minerals are bonded together by a range of complex ferrite-like phases known collectively by the acronym „SFCA“ (Silico-Ferrite of Calcium and Aluminium). These „SFCA“ phases can be divided on the basis of composition and morphology into two main types: one is a low-Fe form that is simply referred to as SFCA [1], and the second is a high-Fe, low-Si form called SFCA-1 [2]. SFCA and SFCA-1 are believed to be the most desirable bonding phases in iron ore sinter because of their high reducibility [3], high mechanical strength and low reduction degradation [4,5], all of which are significant factors in determining the efficiency of the blast furnace. Figure 1a is a schematic showing a typical mixture of iron ore fines, flux and coke, and Figure 1b shows a schematic of ideal iron ore sinter product after the mixture has been heated and cooled. The porous sinter product is used as feed material for the blast furnace. Iron ore fines, however, are not suitable feed material because they significantly decrease the permeability of reducing gases within the blast furnace, which results in low blast furnace efficiency.

![Figure 1: Schematic showing a) a typical mixture of iron ore fines, flux and coke, and b) ideal iron ore sinter product.](image)

Despite their importance in controlling the quality of iron ore sinter, the mechanisms of „SFCA“ formation from precursor phases are not well understood. Increased understanding has the potential to significantly increase the efficiency of the sintering process, by being able to predict optimal sintering conditions (i.e. temperature, oxygen partial pressure and composition) to produce a high quality product. Previous investigations have used either dynamic scanning electron microscopy methods to follow chemical changes [6], or heating/quenching methods in which characterization was conducted ex situ [7]. These studies have all provided important information about the chemical and thermal conditions...
required to form SFCA and SFCA-1. However, investigations using these techniques are unsuited to the study of phase evolution and, therefore, cannot determine the role of intermediate or precursor phases.

In an attempt to understand the role of precursor phases, Scarlett et al. [8] examined SFCA and SFCA-1 formation in situ using X-ray diffraction (XRD) methods. While these studies provided important information regarding the phase changes occurring in the initial stages of sintering, they had limited application to „real” sinter systems as they operated entirely within the solid state region at temperatures below 1250°C. In addition, the experiments were conducted in vacuum and therefore not representative of oxygen partial pressures (pO₂) operating in a sinter plant. In real sintering environments, partial melting occurs at temperatures > 1250°C, and pO₂ values typically range from relatively reducing during the initial stages of sintering as the coke breeze is consumed, to more oxidising pO₂ values during cooling. The current investigation extends the in situ diffraction approach of Scarlett et al. [8], and aims to determine the effect of temperature, Al₂O₃ concentration, CaO:SiO₂ ratio, impurity (MgO) concentration and pO₂ on sinter phase formation. In addition, the temperature range was extended from the original work of Scarlett et al. [8] to beyond the melting point of „SFCA”, and also included a controlled cooling stage to examine the quench phase formation.

Figure 2: Accumulated in situ S-XRD data for one of the sinter mixture samples. Data are shown as a stacked sequence of individual patterns with dataset number (temperature) plotted against 2θ, and with the data viewed down the intensity axis [9]. The diffraction peaks for the starting mixture are annotated with F (Fe₂O₃), C (CaCO₃), A [Al(OH)₃] and α-S (α-SiO₂). Magnetite peaks are annotated with M, and those due to diffraction from the platinum strip are annotated with Pt.

To examine the effect of varying Al₂O₃ content, in situ synchrotron XRD (S-XRD) experiments were performed on synthetic sinter mixture samples containing 1, 5 and 10 wt% Al₂O₃ on the powder diffraction beamline at the Australian Synchrotron. Figure 2 [9] shows accumulated S-XRD data collected for a sinter mixture with composition 77.36 wt% Fe₂O₃ (hematite), 14.08 wt% CaO (added as CaCO₃, calcite), 3.56 wt% SiO₂ (quartz), and 5.00 wt % Al₂O₃ (added as Al(OH)₃, gibbsite). An Anton Paar HTK 2000 high-temperature chamber, with a platinum resistance strip heater was used to heat the sinter mixture samples to 1350°C under pO₂ = 5x10⁻³ atm. The sample was heated at a rate of 20°C min⁻¹ from room
temperature to 600°C (approaching the decomposition temperature of calcite), and then at the slower rate of 10°C min\(^{-1}\) (during the period of SFCA and SFCA-1 formation) up to 1350°C. The sample was then cooled at a rate of 5°C min\(^{-1}\) from 1350°C down to 700°C (during the period of SFCA/SFCA-1 crystallisation from the melt), and then at 20°C min\(^{-1}\) down to room temperature. These heating and cooling rates are substantially slower than would be operating during an industrial sinter process, but the choice of conditions was a trade-off between the time taken to reach temperature and the time required for the collection of individual diffraction datasets. Data were collected throughout heating and cooling, with individual datasets collected for 2 min. Significant events throughout the experiment are numbered on the plot:

1. Decomposition of Al(OH)\(_3\) to an amorphous Al-oxide;
2. Conversion of α-SiO\(_2\) to β-SiO\(_2\);
3. Decomposition of CaCO\(_3\) to CaO;
4. Formation of 2CaO.(Fe\(_2\)O\(_3\))\(_{1-x}\).(Al\(_2\)O\(_3\))\(_x\), \(x < 0.56\);
5. Formation of CaO·Fe\(_2\)O\(_3\) and what appears to be a CaO·(Fe\(_2\)O\(_3\))\(_{1-x}\).(Al\(_2\)O\(_3\))\(_x\) phase;
6. Formation of SFCA-1 and SFCA;
7. Formation of a magnetite (Fe\(_3\)O\(_4\)) and melt phase assemblage;
8. Crystallization of SFCA-1 and SFCA from the melt; and, finally,
9. Transformation of Fe\(_3\)O\(_4\) to Fe\(_2\)O\(_3\) during cooling.

Until now there has been general agreement in the literature that SFCA is the only phase to crystallise from the melt during cooling. Here, however, SFCA-1 is clearly observed to crystallise from the melt. Results also show that Al\(_2\)O\(_3\) concentration has a significant influence on the transformations/reactions evident in Figure 2. In particular, increasing Al\(_2\)O\(_3\) increases the range over which SFCA-1 exists before SFCA starts to form; increases the stability range of „SFCA” during heating and cooling; and suppresses the Fe\(_3\)O\(_4\) \(\rightarrow\) Fe\(_2\)O\(_3\) transformation during cooling. The implications of these observations will be discussed.

**Acknowledgements**

ANSTO is acknowledged for partial funding of this research. This research was undertaken on the powder diffraction beamline (10BM1) at the Australian Synchrotron, VIC, under beamtime awards AS093/PD1639 and AS113/PD4160.

**References**

New Approach to Nitrogen Control in EAF Steelmaking

Geoffrey Brooks\textsuperscript{a}, Gordon Irons\textsuperscript{b} and Dorel Anghelina\textsuperscript{b}
Swinburne University of Technology and McMaster University

High grade steels, particularly in flat products are associated with low levels of dissolved nitrogen. For deep drawing steels it is desirable to keep nitrogen levels below 50 ppm, where as a range of 120 to 150ppm is acceptable for high strength structural steels (1). In EAF steelmaking, molten metal is often exposed directly to the air during the melt down. Ionisation of nitrogen by the arc is also thought to accelerate the rate of nitrogen pick up by the steel. In addition, scrap and ferro-alloys can contain significant dissolved nitrogen. As a result, whist steel produced from Oxygen steelmaking contains 30 to 40ppm, nitrogen levels in steel produce from EAF is typically in the range 70 to 100ppm.

As mini-mill operators have made the move from long products, traditionally associated with EAF production (2), to the more high value flat product range, the issue of nitrogen control has become important. A number of methods have been developed to lower nitrogen, including vacuum treatment, carbon oxidation to produce fine CO bubble to dissolve nitrogen, improving slag cover during melting and dilution with low nitrogen materials such as DRI and pig iron (2, 5). Goldstein et al. (3) studied the effect of adding DRI pellets on the removal of nitrogen from steel. They found that whilst the formation of CO bubble below the melt had the potential to lower the nitrogen level through “flushing” of nitrogen into fine CO bubbles, the buoyancy of DRI pellets reduced this effect, as the bubbles would pass through the slag layer.

Research into the use of iron carbide in EAF steelmaking during the 1990s found that injection of iron carbide nitrogen levels could be reduced from 80 to 30ppm, which was thought to be largely due the flushing effect of very fine CO bubbles travelling through the melt (5). Brooks and Huo (6) investigated the rate of CO generation from different iron carbide sources, as a first step to understanding the flushing effect of iron carbide injection. This line of thinking, that is, the idea that injecting an iron source with CO generating capability into an EAF had the potential to greatly lower nitrogen, lead to an AISI-DOE funded project at McMaster University by the authors of the paper (7, 8 & 9).

It was proposed that DRI fines be injected late in the melting sequence to remove nitrogen before lade treatment. DRI fines are generated from the DRI production processes or by attrition in transport and handling. The study on materials characterisation of the DRI fines, mathematical modelling of the nitrogen removal process and comparison to existing industrial data (7, 8 & 9).

It was found that the most important characteristic of the DRI fines was that the carbon and oxygen contents be balanced stoichiometrically to produce as much CO per tonne of DRI as possible. Ideally, the gangue content of the DRI fines should be minimised to reduce energy requirements for melting and slag volume. These relationships are summarised in Figure 1.
Thermodynamic relationships were developed to predict the level of nitrogen removal for a given level of CO generated from a quantity of DRI. These relationships were used to analyse plant train data from Ispat Hamburger and North Star operations, where a range of DRI fines, lump DRI and scrap feeds were trialled. Whilst, it was difficult to separate nitrogen flushing and dilution effects, the analysis suggested that approximately 25% of nitrogen can be removed from steel with approximately a 5% addition of DRI fines to an EAF (7).

Kinetic analysis of the process was based on the assumption that mass transport on the liquid side at the bubble is much slower than the gas side, that the kinetics could be controlled by adsorption of sulphur and oxygen at the interface and that mass transport of nitrogen from the bulk to the bubble region is no transport limiting. The model included the effect of bubble size and rising distance (i.e. how deep the fines are injected). Typical results are shown in Figure 2. These calculations show that the bubbles can only pick up a few percent of nitrogen during the rise, and that the curves become parallel after some rise time because the bubbles are approaching the equilibrium. The equilibrium content is also varying as the Ferro static head. Please note that very fine bubbles saturate very quickly, so producing the bubbles deeply in the bath is not required. This also means that because the kinetics is fast, a thermodynamic model can be largely used to assess the potential for removal of nitrogen for a given scenario. The practical engineering issues are more about how to ensure that the fine bubbles are evenly distributed in the bath to maximise nitrogen removal. An injection model was developed to allow selection of parameters such as lance diameter, solids feed rate, solid to gas loading and lance angle.
In conclusion, injecting DRI fines late in an EAF melting cycle has the potential to greatly lower the nitrogen level. Further industrial work is required to fully evaluate the concept but existing plant trial data and modelling analysis by the authors indicate that the idea is technically and economically viable.

References

Investigation and Application of Phase Equilibria in the System Al\textsubscript{2}O\textsubscript{3}-CaO-MgO-SiO\textsubscript{2} Relevant to BF Slag

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**Keywords:** BF slag, phase diagram, EPMA, Al\textsubscript{2}O\textsubscript{3}-CaO-MgO-SiO\textsubscript{2}

The blast furnace process continues to be the principal technique used for ironmaking in the world. The major chemical components of the iron blast furnace slag are Al\textsubscript{2}O\textsubscript{3}, CaO, MgO and SiO\textsubscript{2}. Recent years more and more high-Al\textsubscript{2}O\textsubscript{3} iron ores have been used for the ironmaking which results in high Al\textsubscript{2}O\textsubscript{3} concentration in the iron blast furnace slag. Inspection of the compositions of the iron blast furnace slag in Shougang indicated that the Al\textsubscript{2}O\textsubscript{3} concentration in the slag has increased from 7-8 wt\%\textsuperscript{1} in 1980s to 15-16 wt\% now\textsuperscript{2}. Similar trend has been observed in other ironmaking companies\textsuperscript{3-6}. It has been shown during industrial practices that high Al\textsubscript{2}O\textsubscript{3} concentration in the conventionally used iron blast furnace slag significantly increases the viscosity of the slag and results in difficult operation.

To confront the difficulty of high-Al\textsubscript{2}O\textsubscript{3} concentration in the slag and to assist in the optimization of the iron blast furnace operations Shougang has identified the need for a fundamental understanding of the physical and chemical properties of the iron blast furnace slags in the Al\textsubscript{2}O\textsubscript{3}-CaO-MgO-SiO\textsubscript{2} system.

The binary basicities (B2 = CaO/SiO\textsubscript{2}) of Shougang blast furnace slags are around 1.14, 1.18, 1.15 in Jingtang, Qiangang and Shouqin operations respectively. CaO and SiO\textsubscript{2} can be treated as one variable if the CaO/SiO\textsubscript{2} ratio is fixed, and the quaternary system (Al\textsubscript{2}O\textsubscript{3}-CaO-MgO-SiO\textsubscript{2}) can be simplified to a pseudo-ternary system (CaO+SiO\textsubscript{2})-Al\textsubscript{2}O\textsubscript{3}-MgO. The phase diagram (CaO+SiO\textsubscript{2})-Al\textsubscript{2}O\textsubscript{3}-MgO at B2 = 1.1 has been experimentally determined in air.

There are a number of difficulties in obtaining accurate chemical equilibrium data for complex slag systems, for example, accurate measurements of slag composition and equilibration temperature. The experimental procedures developed by Pyrometallurgy Research Centre at the University of Queensland have resolved a number of experimental difficulties and have been successfully applied to a number of complex industrial slags.

The experimental technique for phase equilibrium measurements is based on the high temperature equilibration of the synthetic slag samples followed by quenching. The liquid phase is converted into glass on quenching, and crystalline solids are frozen in place. The quenched sample is then mounted, polished, and compositions of the liquid and solid phases are measured by electron probe X-ray microanalysis (EPMA). The accuracy of temperature is controlled within 5 degrees Celsius, and the accuracy of phase composition measurements is within 1 wt \%\textsuperscript{7}.

It was found that melilite and spinel are major primary phases in the composition range related to iron blast furnace slags. In addition, merwinite and periclase also appear at certain conditions. EPMA measurements show that the compositions of spinel (MgO. Al\textsubscript{2}O\textsubscript{3}),
merwinit (3CaO.MgO.2SiO₂) and periclase are close to their stoichiometry. The melilite is the solid solution of akermanite (2CaO.MgO.2SiO₂) and gehlenite (2CaO.Al₂O₃.SiO₂). Typical microstructures of the quenched samples are presented in Figure 1, showing well-quenched liquid slag in equilibrium with melilite (Figure 1a) and spinel (Figure 1b) respectively.

Figure 1: Typical microstructures of quenched slags from a) melilite and b) spinel primary phase fields in air

Experimentally determined pseudo-ternary section (CaO+SiO₂)-Al₂O₃-MgO with CaO/SiO₂ ratio of 1.1 is shown in Fig.2. Predictions of FactSage 6.2 are also shown in the figure for comparison. It can be seen that FactSage predictions are in good agreement with the present study.

It can be seen from the figure that BF slags in Shougang are located in melilite primary phase field and the liquidus temperatures are between 1410 and 1420 °C. Clearly the liquidus temperatures of the BF slags increase with increasing Al₂O₃ concentration. At a given (CaO+SiO₂)/Al₂O₃ ratio the liquidus temperatures of the BF slags can move in two directions with MgO concentrations.

1) Increasing the concentration of MgO will slightly decrease the liquidus temperature. However, spinel phase will appear at high MgO concentration and the liquid temperatures will increase significantly in the spinel primary phase field. In addition, the slag volume will also be increased as most MgO is added as flux.

2) Decreasing the concentration of MgO can also decrease the liquidus temperature. In the other word, the liquidus temperatures can be kept the same for high Al₂O₃ slag if MgO concentration is decreased. In this way the slag volume can also be reduced. This will be the strategic direction proposed to BF operators.
Figure 2: Pseudo-ternary section (CaO+SiO₂)-Al₂O₃-MgO with CaO/SiO₂ ratio of 1.1 in air

References

Metals and Enabling Sustainability

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Metals are an essential component of today’s society: a moment’s reflection on their ubiquitous presence in virtually all energy and material production processes is enough to confirm this. We also, of course, consider an abundant supply of clean water a routine essential, and the constant need for energy is a given all over the world. However, the resources of our planet are limited, as is the strain to which we can subject it in terms of emissions, pollution, and disposal of waste. For these reasons, finding ways to lower the environmental footprint of our collective existence and therefore lowering greenhouse gas emissions and help mitigate climate change [Santer et al., 1996 & IPCC, 2007] is a vital priority.

This urgent need highlights Outotec’s status as a vital player in sustainability. Two things are required: the best available technology for reducing the environmental toll of existing processes, and innovative solutions to reverse the trend on a global scale. With our decades of experience and forward-looking attitude, we see ourselves as capable of fulfilling both of these criteria, enabling sustainability as a company by providing metals for products that lower society’s environmental footprint.

Closing the loop

At Outotec, we produce some of the world’s most energy-efficient metals and water processing solutions, often making extensive use of local resources and personnel. We are justifiably proud of our sustainability track record in process technologies. However, our activities do not end there. The ultimate aim of our solutions is to decouple resource usage, and thereby the welfare of our societies, from nature. This is achieved through advanced metal recovery, water and recycling technologies.

It may surprise you to learn that for some metals, recovery has already eclipsed mining as the principal source for production. Lead is a good example, as over 50% of the metal currently produced worldwide is sourced from recycled car batteries. Outotec’s top submerged lance technology helps to make this possible, and can be used to process and recover other metals, as well as e-waste.

Resource efficiency [EU, 2011 & Reuter, 2011] is of great importance when considering the production of metals from this perspective. Prudent and efficient use of materials and technology will define our future on this planet, and, by recognizing this fact today, we are taking a responsible step towards ensuring that the preconditions for an advanced society continue to be available for generations to come.

Enabling sustainability

As we strive to make clear, Outotec’s commitment to sustainability extends far beyond our own operations, which are relatively minor in terms of emissions. We see our impact in the
mining and metallurgical industries as of core importance to the effective use of the planet’s limited resources.

You may have seen the phrase “enabling sustainable use of Earth’s natural resources” in an Outotec publication. This statement is testament to the fact that we not only seek to produce metals sustainably, but also aim to provide the materials necessary for green energy production methods such as solar and wind power, as well as other energy-conserving solutions like mass transport concepts. All of these are means of reducing our footprint as a global society, and all, for better or worse, require metals from the outset. The key fact is that we want those metals to be produced in a sustainable manner, and then returned to the value chain via recycling once they have achieved their purpose in the world.

Take wind power, for example. Those impressive windmills one can seetowering over the shorelines of some of our most forward-thinking countries are constructed mainly of steel, and the magnets employed within them incorporate rare earth elements. It must be recognized that without the mining and metallurgical industries, the resource-efficient solutions of the near and far future will simply not come to pass.

**Consumer expertise**

A company cannot provide metallurgical solutions effectively without deep insight into the fields in which the end product will ultimately be used nor without substantial knowledge of consumer demands. Every quantity of metal produced using Outotec technologies will end up with a consumer of some kind, and knowledge of how they will employ these materials is one of the best ways in which we can promote resource efficiency (Figure ). Understanding both the design and the substance well can lead to enterprising new whole-of-system solutions and techniques to impact sustainability significantly. Again, Outotec has a unique opportunity to offer its expertise here, for the greater benefit of our society.

There is also a more wide-ranging perspective, of equal or greater importance, which involves seeing where society’s usage of metals is headed, anticipating trends in sustainable solutions, and ensuring that the materials in demand in the future are put to good, efficient use before them, too, reenter the production cycle. We at Outotec, for our part, will continue working to ensure that the fundamental link between metals and sustainability is handled with awareness, experience, and significant expertise. In doing so, we hope to help guarantee a sustainable future for our planet.

**Outline of Presentation**

Figure 1 will be the leitmotiv of the presentation and will be discussed in the abovementioned context. Resource Efficiency will among others be discussed in terms of the optimal link between primary metal production and recycling of end-of-life consumer goods via the optimization of recycling and production systems, while maximizing water recycling and minimizing losses through among others residue and sludges creation from primary ore extraction as well as “urban” mining activities. Of interest, therefore, are also Design for Recycling and Sustainability [Reuter, 2011]. Linking simulation and environmental impact software such as PE-International”s GaBi (www.peinternational.com) and Outotec”s HSC Sim (www.outotec.com) will help much to improve the environmental impact of metal production, recycling and Design for Recycling and therefore also help to maximize Resource Efficiency. The extraction and recycling of sustainability enabling metals, materials
and their compounds used in renewable energy production infrastructure, battery technology, sustainable transport, smart sustainability enabling IT systems, are among others of key importance and will also be discussed. The context of this presentation also gleans from a United Nations Environmental Programme [UNEP, 2012] the presenter is the lead author of.

References


![Resource Efficiency Diagram](image_url)

Figure 1: Resource Efficiency – Among others optimally linking mining, minerals processing, primary and secondary extractive metallurgy, energy recovery, OEMs & product design, end-of-life products, recyclates, residues, wastes; while minimizing resource losses and maximizing water and air quality.
Greenhouse Gas Emission Assessment of Bio-coke from Wood for Application as Bioanode in Aluminium Production

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Key words: bioanode, GHG emission, LCA, aluminium, carbon footprint

In aluminium reduction cells, carbon anodes are used for electrolysis. Petroleum coke is the primary source of material used in the manufacture of these anodes. There is a trend of falling quality of petroleum coke and the level of impurities is also increasing. This is particularly concerning to the aluminium industry because this reduces the anode performance, contributes to corrosive gases in the exhaust stream, and contaminates the aluminium metal product. These supply issues, combined with an increased awareness and preparedness to reduce greenhouse gas (GHG) emissions, opens the aluminium industry to the possibility of replacing fossil-based carbon anodes with low ash, renewable carbon based biocoke. The biocoke is to be used for making anodes known as „bio-anodes” (de Vries et al., 2009). Our research has highlighted that viable anode grade petroleum coke requires a density of 800 kg/m³. This is possible using a CSIRO patented technology of bio-coke making. This process requires high temperature pyrolysis of wood under mechanical compressive force.

The bio-anode is expected to be made from bio-coke that is converted from biomass using the above mentioned process. Wood can be sourced from either plantation or natural forests. In this study, the biomass of choice is pine wood from an established plantation, as approximately 65% of the forestry industry in Australia is plantation based. This share is steadily growing over time. There are several silvicultural management practices routinely undertaken during the establishment and growth phase of plantation estates. These unit processes require materials, thermal and/or electrical energy generally derived from non-renewable energy sources. Thus, there is a need to determine life cycle assessment (LCA) based GHG emissions. The boundary includes the tree growth, harvesting, collection, transport, processing to pyrolysis process to make bio-coke and convert it to bio-anodes. The purpose of this paper is to report GHG footprint of biomass processing and coke making according to the guidelines provided in the international standards (ISO, 2006).

The calculated total non-renewable (i.e. fossil fuel and material use) GHG emission footprint of bio-coke production was 50 to 155 kg CO₂ equivalent per tonne (eq/t) of bio-coke for the best and worst case scenarios, respectively. The GHG footprint of anode grade petroleum based coke is about 402 kg CO₂ eq/t (Figure 1). Both numbers have an overall ±10% uncertainty based on input data quality assessment. The best case scenario assumed the use of hydro-electricity in the production.
Based on an LCA, the total GHG emission was calculated to be 24,700 kg CO₂ eq/t of primary aluminium produced using the average emission factor for Australian electricity. Depending on blend ratios of petcoke with bio-coke, this emission intensity can be reduced. For a 100% substitution with bio-coke, this is 23,100 kg CO₂ eq/t Al, or 6.5% reduction. For a hypothetical plant of 250,000 tpa aluminium production capacity, there is an opportunity to reduce 400,000 t of CO₂ eq per year. This is equal to $9.2 million credit or tax saving assuming $23/t CO₂ price under a carbon trading or tax scenario. However, utilisation of this opportunity requires the establishment of a pyrolysis and bio-coke plant with associated infrastructure and investment. With this investment, there may be other socio-economic benefits from having a sustainable plantation industry and with the creation of new regional jobs.

References:


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Electrochemical Slag-Metal Reaction for Silicon Production
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Silicon is an important semiconducting and photovoltaic material. It is also widely used for chemical and metallurgical applications. The rapid growth in the demand of solar photovoltaic (PV) cell results in the shortage of solar-grade (SOG) silicon feedstock. Expensive scrap electronic grade (EG) silicon (99.999999% Si) is commonly used as the raw material to produce SOG-Si (99.9999% Si). Many researchers have reported that relatively inexpensive metallurgical grade (MG) silicon (98-99% Si) can be used as an alternative raw material for refining of MG-silicon to produce SOG-Si.

The slag treatment on MG-Si for SOG-Si production is based on the principle of liquid-liquid extraction in steel industry. The slag used for the extraction of impurities must dissolve individual impurities better than molten silicon does, the solubility of silicon in the slag must be low, and the slag must be nonreactive with molten silicon and must differ markedly from it in density. The impurities with a higher oxygen affinity in comparison with silicon oxidize and pass into the slag. The process is particularly attractive for reducing the B and P content in the production of SOG-Si. In this method, liquid silicon is treated with CaO-SiO₂, CaO-SiO₂-CaF₂, CaO-SiO₂-Al₂O₃, CaO-SiO₂-Al₂O₃-MgO and other molten slags [1-2].

As known from literature [1-2], the partition ratio of boron between CaO-SiO₂ slags and liquid Si is between 2 and 5, what makes it possible to remove boron from silicon using chemical equilibration by slag. The idea is to enhance this process electrochemically, by using the Si-B liquid as an anode. Let us consider a liquid metal / molten slag two-phase system, with at least two components in both phases (they can contain more components): Si-B and SiO₂-B₂O₃. Let us suppose first chemical equilibrium in the system, with an equilibrium partition ratio of boron, \( L_{B}^{\text{eq}} \) defined as the ratio of the mole fractions of boron oxide in slag to boron in metal. By applying an anodic potential to the Si-B alloy, \( \Delta E \), it can connected to the partition ratios as:

\[
\Delta E \approx \frac{R \cdot T}{3 \cdot F} \cdot \ln \left( \frac{L_{B}^{\text{eq}}}{L_{B}^{\text{eq}}} \right)
\]  

(1)

The sign of approximation means that we suppose diluted solutions of B in liquid metal and diluted solution of B₂O₃ in slag, i.e. we suppose the constancy of their activity coefficients, what is only an approximation. \( R = 8.3145 \) J/mol.K, \( F = 96485 \) C/mol, \( T \) in K. From Eq.(1) the requested value can be expressed as:

\[
L_{B} \approx L_{B}^{\text{eq}} \cdot \exp \left( \frac{3 \cdot F \cdot \Delta E}{R \cdot T} \right)
\]  

(2)

The calculated values are shown in figure 1. One can see that the partition ratio increases fast with applied potential.

The experiments were carried out in a vertical tube furnace with four Mo-Si resistance heating elements in this study to check the electrochemical behaviour of slag-metal reaction.
The schematic diagram is shown in figure 2. The top and bottom part of the furnace were designed so that they can suspend a crucible and also allow electrodes to be introduced from the top part of the furnace into the crucibles. Materials chosen for the anode and cathode electrodes required are Tungsten (W) (1.6 mm) and Molybdenum (Mo) (2 mm) respectively. High purity argon gas was used during the experiments. This is to ensure that the atmosphere condition in the furnace has very low moisture and oxygen content during experiment at 1550°C. Slag of about 12 gm with 8 gm Silicon alloy (Si-B) was placed in an alumina crucible. The crucible was suspended in the furnace using an alumina pedestal from the bottom. The cathode wire was sheathed with alumina tube to avoid the contact with molten silicon. The anode was sheathed with alumina tube to avoid the contact with species (Si vapour or SiO vapour). A multimeter was used to measure the open circuit voltage (OCV) and it was connected with conduction wires. The experimental result is shown in figure 3. The experimental potential value is lower than the FactSage prediction but experimental result shows that slag-metal reaction involves electrochemical means.

![Figure 2: Schematic diagram of experimental setup](image)

![Figure 1: The dependence of the partition ratio of boron on the applied anodic potential calculated by Eq. (2) using \( L_{u} = 3 \), \( T = 1823 \) K.](image)

![Figure 3: The potential difference (\( \Delta E \)) between slag and metal with time.](image)

### References


Integrating Solar Thermal Technology into the Australian Minerals Processing Industry

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Key words: minerals processing, high temperature, solar thermal

Introduction
Opportunities for thermal integration of solar technologies into the Australian minerals processing industry are being considered to reduce Australia’s reliance upon non-renewable fuels and decrease greenhouse gas (GHG) emissions of the industry. For the purpose of this study, the Australian minerals processing industry is defined as: “all process plants located in Australia producing metallic or mineral products but excluding coal, gas and oil processing facilities.” This definition includes mineral concentration facilities as well as smelters and refineries. Due to the lower temperature requirements of mineral concentration plants, the initial interest has been on smelters and refineries. Emphasis was given to five sub-industries that generate a large portion of the total GHGs – aluminium and alumina, iron and steel, cement, nickel and, copper.

Solar Thermal Technology Status
There are a number of technologies for the concentrating of solar heat; linear receivers such as parabolic troughs and linear Fresnel; and point focus systems such as central receiver towers and the parabolic dishes. Solar towers consist of a large array of heliostats (sun-tracking mirrors) which focus the sun’s rays onto a central tower. Early tower developments have produced temperatures around 500 to 800°C although they can achieve 1000°C or more. Parabolic dishes can also achieve very high temperatures of 500 to 1600°C at the focal point of the dish. Two solar towers capable of producing temperatures of more than 900 °C are located at the CSIRO’s Energy Centre, Newcastle where proof-of-concept for solar generated synthesis gas or SolarGas™ (CO + H₂) (Figure 1) has been achieved and the Brayton Cycle for electricity generation is being investigated.

![Figure 1: CSIRO's heliostat field and tower for concentrating solar thermal energy for the production of SolarGas™.](image)

<table>
<thead>
<tr>
<th>Solar Thermal Collector Type</th>
<th>Temperature range</th>
<th>Common use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parabolic Trough</td>
<td>400</td>
<td>Steam and electricity</td>
</tr>
<tr>
<td>Linear Fresnel</td>
<td>400</td>
<td>Steam and electricity</td>
</tr>
<tr>
<td>Central Receiver Tower</td>
<td>500 → 1000</td>
<td>High temperature reaction vessels</td>
</tr>
<tr>
<td>Parabolic Dish</td>
<td>500 → 1000</td>
<td>Stirling heat engines and other very high temperature applications</td>
</tr>
</tbody>
</table>

Table 1: Summary of the Current Status of Solar Thermal Technology

Greenhouse Gas Emissions
The Australian minerals processing industry generated more than 8% of Australia’s total GHG’s in 20093. Based on 2010 National Greenhouse and Energy Reporting (NGER) data2, Table 2

<table>
<thead>
<tr>
<th>Product</th>
<th>GHG emissions as percentage of total direct and indirect (%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum and Alumina</td>
<td>15 48</td>
<td></td>
</tr>
<tr>
<td>Iron and Steel</td>
<td>33 25</td>
<td></td>
</tr>
<tr>
<td>Cement</td>
<td>15 10</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>5 3</td>
<td></td>
</tr>
<tr>
<td>Misc (Cu, Au, U, Ag, Zn, Ni)</td>
<td>1 3</td>
<td></td>
</tr>
<tr>
<td>Titanium</td>
<td>2 2</td>
<td></td>
</tr>
<tr>
<td>Zinc</td>
<td>1 2</td>
<td></td>
</tr>
<tr>
<td>Gold</td>
<td>1 2</td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>2 1</td>
<td></td>
</tr>
<tr>
<td>Others</td>
<td>3 4</td>
<td></td>
</tr>
</tbody>
</table>

Table 2 - Breakdown of GHG emissions by individual industries as a percentage of the total GHG emissions2.
displays the breakdown of the total GHG emissions in the Australian minerals processing industry.

**High Temperature Processes with Potential for Solar Thermal Integration**

The processes which have a process step at a suitable temperature for solar thermal technologies are summarised in Table 3.

<table>
<thead>
<tr>
<th>Metal/Mineral</th>
<th>Location</th>
<th>Process</th>
<th>Temperature</th>
<th>Current Fuel</th>
<th>Particle size (mm)</th>
<th>Potential Solar Thermal Integration</th>
<th>Approx. % of total individual plant GHG emissions</th>
<th>Approx. % of Aus. minerals processing GHG emissions</th>
<th>Atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina</td>
<td>Various</td>
<td>Calculing</td>
<td>1000 → 1100</td>
<td>natural gas (NG)</td>
<td>0.02 → 0.2</td>
<td>Solar kiln</td>
<td>30</td>
<td>14.4</td>
<td>-</td>
</tr>
<tr>
<td>Iron</td>
<td>Various</td>
<td>Reducing</td>
<td>2000</td>
<td>coke pellets</td>
<td>Use DRI processes</td>
<td>30-35</td>
<td>11.75</td>
<td>reducing</td>
<td></td>
</tr>
<tr>
<td>Cement</td>
<td>Various</td>
<td>Calculing</td>
<td>1450</td>
<td>coal</td>
<td>1 → 5</td>
<td>Solar kiln (at 1000°C)</td>
<td>35 (≤ 90 including CO2 released chemically)</td>
<td>3.5 (≤ 9)</td>
<td>-</td>
</tr>
<tr>
<td>Nickel</td>
<td>Yabulu</td>
<td>Calculing</td>
<td>1100</td>
<td>coal</td>
<td>Solar kiln</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Yabulu</td>
<td>Reduction</td>
<td>750</td>
<td>heavy fuel oil</td>
<td>Syngas</td>
<td>-</td>
<td>-</td>
<td>reducing</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Kalgoorlie</td>
<td>Air Pre-heat</td>
<td>450</td>
<td>coal</td>
<td>Solar heater</td>
<td>≤ 5</td>
<td>0.15</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Kalgoorlie</td>
<td>Flash Furnace</td>
<td>1200 → 1500</td>
<td>coal and fuel oil</td>
<td>molten Syngas</td>
<td>≥ 40</td>
<td>1.2</td>
<td>reducing</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Kwinana</td>
<td>gas reforming for ammonia syngas</td>
<td>900</td>
<td>NG → ammonia and hydrogen</td>
<td>gas</td>
<td>Solar reforming</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Copper</td>
<td>Olympic Dam</td>
<td>Andore furnace</td>
<td>1100 → 1200</td>
<td>sulfur compounds in nickel</td>
<td>molten Syngas</td>
<td>10</td>
<td>0.1 - 0.2</td>
<td>oxidising or reducing</td>
<td></td>
</tr>
</tbody>
</table>

Table 3 - Summary of high temperature processes in the Australian minerals processing industry which may have potential for solar thermal integration either directly or indirectly.

**Calcining – Thermal Decomposition**

- **Alumina:** Calcining of „wet“ alumina to form anhydrous alumina generates about 30% of the total GHG emissions in the Australian aluminium-alumina industry (Figure 2) and about 14% of the total GHG emissions from the Australian minerals processing industry. The peak operating temperature is 1000 to 1100°C.

- **Cement:** The fuel used in the calcining of limestone (CaCO3) generates about 35% of the total cement industry GHGs with the remainder being mostly the CO2 chemically released from the limestone.

The commercial operating temperature is about 1450°C in a horizontal rotary kiln. Limestone can be effectively calcined at lower temperatures (≥1000°C).

- **Nickel:** The product of the leaching process (nickel carbonate, NiCO3) is calcined to produce nickel oxide (NiO). The peak operating temperature is 1200°C.

**Demonstration Project:** The temperatures of the calcining processes are in the appropriate range for solar thermal integration. Meier et al (2006) designed a kiln for the solar production of lime (and thus cement) (Figure 3). The kiln developed by Meier et al has been designed to:

- calcine limestone at about 1000°C and 1 bar,
- hybridise with conventional fuels,
- achieve 98% calcination at a flow rate of 2 to 8 kg/hr in a 10 kW experimental set up and,
- be scaled up for industrial use.
It may be compatible with other processes such as the calcining of alumina or nickel carbonate. The operating temperatures and particle sizes are similar in all three cases.

**Reduction in Furnaces**

- **Iron:** The iron oxide in iron ore is reduced to pig iron in blast furnaces at very high temperatures (~2000°C). The blast furnace contributes about 50% of OneSteel’s GHG emissions and at least 70% of BlueScope Steel’s energy demands. This equates to more than 12% of the Australian minerals processing industry’s total GHG emissions.

- **Nickel:** Nickel oxide (NiO) is reduced to nickel metal (Ni) with ammonia synthesis gas (N₂ and H₂) (generated from natural gas or coal seam methane and water) or the gas resulting from coal or heavy fuel oil combustion as the reducing agents. The peak operating temperature ranges from 750°C to 1350°C.

- **Copper:** Copper oxide is reduced to copper metal in an anode furnace by the addition of fuel gas to the molten copper mixture. It is unlikely that it would be helpful or practical to substitute the fuel gas for syngas. The peak operating temperature is 1100 – 1200°C.

**Analysis of Potential:** Nickel and copper reduction currently operates at suitable temperatures for solar but iron reduction operates at temperatures that are too high for solar technologies. SolarGas™ or syngas contains 25% more energy than the natural gas used to produce it, is a good reductant and can be produced at about 900°C in a solar thermal tower.

- Syngas can be used as a reductant instead of coal or oil in certain processes. For example, it could be used in some furnaces or processes requiring a reducing atmosphere.

- Direct reduced iron (DRI) can be produced with syngas at relatively low temperatures (~1000°C). This would require new plants but could enable more effective integration of solar thermal technology.

- Ammonia synthesis gas can be produced with solar heat and would be useful for nickel reduction in existing plants and ammonia production.

**Outlook**

A number of processes in the Australian minerals processing industry operate at temperatures suitable for solar thermal applications. Individual processes need to be assessed on a case-by-case basis to determine the viability of the solar thermal option based on cost, market and location. Hybridising solar thermal with conventional fuels can be achieved as evidenced by the solar kiln designed by Meier et al (2006). Syngas with a higher calorific value than natural gas can potentially be integrated into existing infrastructure for natural gas. Electricity and/or steam could be produced alongside SolarGas™ with the same solar field. CSIRO has world-class solar thermal facilities in Newcastle that can be adapted to prove the concept for a range of high temperature solar thermal applications such as the mineral processing technologies discussed in this paper.

**References**

Modelling and Simulation of Blast Furnace Ironmaking

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An ironmaking blast furnace (BF) is a complex multiphase flow reactor involving gas, powder, liquid and solid phases. Understanding the flow behaviour of these phases is of paramount importance to the control and optimization of the process. Mathematical modelling, often coupled with physical modelling, plays an important role in this development. This talk will present an overview of work in this area in the past 20 years or so in his Laboratory for Simulation and Modelling of Particulate Systems (SIMPAS) at UNSW in collaboration with Bluescope Steel and other steel companies, covering the formulation, validation and application of mathematical models for gas-solid, gas-liquid, gas-powder and multiphase flows in different zones in a BF, and their incorporation into a process model that can be used to predict the BF flow and performance. The need for further developments is also discussed.

Representative publications

The Solubility of Gold in Metallurgical Slags

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RMIT University

The solubility of gold in slags is of interest to researchers because gold/metal alloys are often used in distribution experiments as a way of correcting for metal entrainment in the slag. Gold is assumed to have negligible solubility in slags, on the basis that the Gibbs free energy of formation of gold oxides is very positive, so any gold found in the slag must be from entrained metal droplets. Toguri and Santander\(^5\) reported that gold solubility in iron silicate slag was up to 800 ppm. Altman & Kellogg\(^6\) used a Cu/Au alloy to determine the solubility of copper in iron silicate slag while Grimsey & Biswas\(^7\) determined the solubility of nickel in the same slag. They both erroneously quoted from Toguri & Santander that gold solubility was less than 80 ppm. Nagamori and Mackey\(^5\) made the same mistake and also claimed, without evidence that gold dissolves as neutral atoms in slag. Celmer and Toguri\(^7\) found the solubility of gold in an Al\(_2\)O\(_3\)-saturated iron silicate slag to be only 25–30 ppm. They assumed gold was present as neutral atoms. Gold solubility in slag is also an issue in fire assaying which involves, at one stage, gold in contact with molten PbO. If gold solubility in molten PbO is not zero then the fire assay result would be understated. Strangely, nothing was found in the literature relating to the solubility of gold in PbO slag. In this work gold solubility in iron silicate and calcium ferrite was determined by equilibrating approx. 5 g of slag and 5 g of gold in a small alumina crucible with CO-CO\(_2\) gas mixtures at 1300°C. Gold solubility in PbO-SiO\(_2\) slags was determined at 1100°C using oxygen/nitrogen gas mixtures. After 8 hours the crucible was lowered into the cool part of the furnace. The slag, gold and crucible were separated and cleaned then the slag was analysed by neutron activation analysis. The minimum detection limit for gold was 0.005 ppm. The results for iron silicate (■) and calcium ferrite (□) have considerable scatter, but it is clear that there is no significant difference in gold solubility in the two slags. There is a clear dependence of gold solubility on the oxygen partial pressure so gold cannot be present in the slags as neutral metal atoms. The slope of the "best fit" line is 0.35, subject to considerable error. This suggests that gold is in the slags as Au\(^+\) ions, for which the slope should be 0.25. The solubility of gold in molten PbO is over an order of magnitude higher than for iron silicate and calcium ferrite slags. The data conforms to a straight line with a slope of 0.23, again suggesting that gold is present as Au\(^+\) ions. The solubility of gold in the PbO-SiO\(_2\) slag system was also determined and it was found that gold solubility is a very strong function of the basic oxide content of the slag, as previously observed by Sano and Nakamura for platinum. The number of oxide ions from the slag associating with a single gold could in principle be determined by plotting the logarithm of the gold content of the slag as a function of the logarithm of the activity of oxide ions in the slag. The Kapoor-Frohberg\(^7\) model was used to calculate the fraction of oxide ions (N\(_{O2^-}\)) in the slag and it was assumed that the activity of oxide ions is proportional to this ion fraction. It was shown that two oxide ions associate with one Au\(^+\) ion in this slag.
References

Behavior of Impurities in Chlorination of Reduced Murray Basin Ilmenite

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\textbf{Keywords:} Murray Basin ilmenite; chlorination; impurity

Technology for titanium metal production includes chlorination of stable oxide TiO\textsubscript{2} in the presence of carbon at 800 - 1100\textdegree C to produce TiCl\textsubscript{4}. The high temperature chlorination is conducted in a fluidized bed and requires a TiO\textsubscript{2}-enriched, low impurity feed. At these temperatures, impurities in the upgraded feed are also chlorinated which imposes strict limit to the contents CaO, Cr\textsubscript{2}O\textsubscript{3}, MnO, MgO\textsubscript{2}, etc. whose chlorination products may collapse the fluidised bed operation. Titanium oxycarbide/oxycarbonitride compounds can be chlorinated at much lower temperatures (200 - 350\textdegree C) [1]. In the low temperature chlorination, impurities either do not chlorinate or chlorinate very slowly [2].

Conversion of titania in synthetic rutile or ilmenite ores into titanium oxycarbide requires 1200 - 1400 \textdegree C [3] while synthesis of titanium oxycarbonitride can be implemented at 1150 - 1300 \textdegree C [4]. Crucial to the development of a viable alternative technology for processing of titanium minerals is the behaviour of impurities in the ilmenite ore in reduction and chlorination reactions. The primary impurities in Murray Basin ilmenite concentrate and their behavior in reduction under N\textsubscript{2} were reported previously [5].

This paper examines the behavior of key impurities in a typical Murray Basin ilmenite ore during carbothermal reduction/nitridation in a H\textsubscript{2}-N\textsubscript{2} mixture and during chlorination. The major mineral phases in the Murray Basin concentrate were pseudorutile (Fe\textsuperscript{2+3},Ti\textsubscript{1}O\textsubscript{6}), rutile (TiO\textsubscript{2}), primary ilmenite (FeTiO\textsubscript{3}), and the main impurity phases were chrome-rich spinels of variable composition ([FeMg][AlCr]\textsubscript{2}O\textsubscript{4}), quartz and zircon (ZrSiO\textsubscript{4}). A minor amount (<1-2\%) of unidentified aluminosilicate mineral phases were also detected. The primary elemental impurities in the ore were iron, chromium, magnesium, manganese, aluminium, silicon and zirconium.

The ilmenite concentrate was wet mixed uniformly with graphite with a C/O molar ratio of 1.5 then dried. The mixture was carbothermally reduced in a horizontal furnace, in a 50 vol\% N\textsubscript{2}-50 vol\% H\textsubscript{2} gas mixture at a flow rate of 1 L/min, at 1150 \textdegree C for 3 h. After reduction the reduced sample was analyzed by combined XRD, LECO, SEM/EDS and EPMA methods.

XRD pattern showed the apparent phases were titanium oxycarbonitride, metallic Fe, and free carbon after reduction. The LECO data indicated only around 2-3\% of total O was left in the reduced sample. The data and images from SEM/EDS and EPMA methods confirmed that the titanium oxides were reduced to titanium oxycarbonitride, the iron oxides in pseudorutile and ilmenite were reduced to metallic Fe, iron phase in chromite-spinel was reduced and formed
alloy together with chromium and carbon. Mg-rich chrome spinel was partially reduced while zircon, quartz and aluminosilicate were not reduced or reduced to a very low extent during this process.

The reduced sample was chlorinated in Cl₂ at 200, 300 and 400 °C for 1 h. Two scrubbers containing a 32% HCl solution were applied to absorb the chlorides. In order to monitor the extent of chlorination of different elements in the reduced ilmenite, liquid samples were taken from the scrubbers every 10 min. The residue left in the reactor was washed, dried and analyzed by SEM/EDS. Filtrates from washing residue were analyzed by ICP-OES.

The extent of chlorination of different impurity elements was calculated as the ratio of the elements' mass in the form of soluble compounds (chlorides) to the total mass of individual elements in a reduced sample before chlorination. Chlorination curves for titanium, iron and chromium are shown in Figure 1.

![Chlorination curves for titanium, iron and chromium](image)

Figure 1: Extent of chlorination of Ti, Fe and Cr vs time during the chlorination of the carbothermally reduced Murray Basin ilmenite ore at 200, 300 and 400 °C

Chlorination of Ti was faster in comparison with Cr and Fe. The chlorination of Ti was finished in 20 min. However, the extent of Ti chlorination was lower, only 78% at 200 °C and increased with increase in temperature, reaching 92% at 400 °C. Chlorination of Fe was slower than Ti but much faster than Cr. The extent of Fe chlorination approached 100% in about 40 min at 200 °C and 25 min at 400 °C. After chlorination, various elements distributed in three locations: dissolved in the scrubbers (SS₁), condensed on the sample boat and reactor tube in compounds, which were soluble in acid and were collected by washing the boat and reactor (SS₂), and left in the residue. The residue was separated into chlorides soluble in acid which was collected in the filtrate after washing the residue (SR), and insoluble compounds in the residue (ISR). Based on mass balance:

\[
M = SS₁ + SS₂ + SR + ISR = SS + SR + ISR
\]  

(1)
The extent of chlorination was defined as

\[ X = \frac{(SS + SR)}{M} \times 100\% \]  

(2)

The extent of chlorination and distribution of different elements, calculated from the ICP-OES data, is presented in Table 1, where the ss% refers to the fraction of an element as evaporated chloride (SS$_1$ + SS$_2$) in the total chlorinated amount of the element, whereas the sr% refers to the fraction of the chloride left in the residue.

Table 1: Extent of chlorination and distribution of chlorinated elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Ti</th>
<th>Fe</th>
<th>Cr</th>
<th>Mn</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>T, °C</td>
<td>200</td>
<td>300</td>
<td>400</td>
<td>200</td>
<td>300</td>
<td>400</td>
<td>200</td>
<td>300</td>
</tr>
<tr>
<td>Extant, %</td>
<td>76</td>
<td>84</td>
<td>92</td>
<td>98</td>
<td>100</td>
<td>100</td>
<td>84</td>
<td>100</td>
</tr>
<tr>
<td>ss, %</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>63</td>
<td>94</td>
<td>100</td>
<td>89</td>
<td>78</td>
</tr>
<tr>
<td>sr, %</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>37</td>
<td>6</td>
<td>0</td>
<td>11</td>
<td>22</td>
</tr>
</tbody>
</table>

According to the ICP data, all the chlorinated Ti reported to the scrubber solutions due to the low boiling point of TiCl$_4$ (136 °C), which also showed a high extent of Ti reduction. The fraction of chlorinated Fe evaporated from the boat increased with increasing temperature, and Fe in the Fe-C and Fe-Cr-C alloys were completely chlorinated. SEM/EDS data confirmed that after chlorination, the carbon frame in the alloy structure was left while Fe and Cr were removed. With the presence of O, C and Cl, the chlorination of Cr was complicated; the chlorination product could be CrCl$_3$ or CrO$_2$Cl$_2$. The boiling point of CrO$_2$Cl$_2$ is as low as 117 °C, while CrCl$_3$ decomposes at 1300 °C and sublimes at 950 °C. Incomplete evaporation of chlorinated Cr at 200 and 300 °C shows that part of Cr was chlorinated to CrCl$_3$. At 400 °C, all the chlorinated Cr was as chromyl chloride, which went directly into the two scrubbers. The extent of chlorination of Mn and its sr fraction decreased with increasing temperature. The boiling point of MnCl$_2$ is 1225 °C, which was not vaporized at the chlorination temperature. Therefore, some manganese chlorides, which formed in the chlorination process, had a low boiling point. The extent of chlorination of Mg, Al and Zr was quite low, which indicated that Mg, Al and Zr were not reduced or reduced to a very low extent before chlorination which is consistent with the reduction data. The extent of Si chlorination showed that SiO$_2$, which cannot be chlorinated at a low temperature, was reduced partially before chlorination. The boiling point of SiCl$_4$ is 57 °C, at the chlorination temperature, all the silicon chloride should be in the scrubber. The sr % indicated that there was other reaction of Si within the residue.

References

Oxidation of Molten Aluminium

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**Keywords:** oxidation, aluminium, kinetic model

Oxidation is a significant source of material loss in the production of primary aluminium, with estimates ranging up to \(\sim 1\%\) of metal loss due to oxidation. An understanding of the fundamental oxidation mechanisms is necessary to develop a kinetic model of oxidation behaviour. Studies of aluminium oxidation have traditionally been thermogravimetric and carried out in a controlled atmosphere furnace. However, it is known that this technique is sensitive to the initial condition of the oxide present on the feedstock \(^1\). This has led to significant variations in data reported in the literature, making modelling problematic.

An experimental technique has been developed to address this limitation, based on earlier work by Freti et al \(^2\), in which the oxide is “skimmed” off of the surface of an open melt to give an effectively pure aluminium surface. The melt surface was skimmed at regular intervals and the skimmed material was processed in a molten salt flux at 750°C to separate the metal from the oxide. The recovered aluminium metal was weighed and the amount of oxide was then calculated by difference.

Experiments were carried out on a melt of commercial purity aluminium exposed to ambient air. The melt surface area was \(\sim 0.05\) m\(^2\) (approximately the size of an A4 piece of paper). Oxide samples were taken at melt temperatures of 750, 850, and 900°C after holding times ranging from 30 seconds to 8 hours. Figure 1 shows the amount of oxide formed, in g/m\(^2\), as a function of the holding time at the three temperatures.

The amount of oxide formed increased with both time and temperature, and the oxidation rate at 850°C was greater than at 750°C. The data at 750 and 850°C can be described reasonably well by a power law relationship, within experimental error, indicating a continuous reduction in oxidation rate over time, although the 900°C data is currently too limited to make a similar observation.

Overall, very little oxide formed on the aluminium melt, significantly less than what forms in an industrial setting. This suggests that there are other factors more significant than time and temperature that influence the oxidation behaviour under such conditions.

Preliminary microstructural characterisation of the oxide using TEM has shown the presence of angular crystallites up to several tens of nm in size, within or on an amorphous matrix. Corresponding electron diffraction patterns show ring patterns rather than discrete spots, characteristic of an amorphous (or very fine polycrystalline) phase. The rings are often discontinuous and present as a series of arcs, indicative of a textured material, suggesting that the oxide crystallites are present in certain preferred orientations. A more complete...
description of the oxide will be able to be developed pending further systematic characterisation of samples taken at various times and temperatures.

Figure 1: Mass of oxide per area formed on a quiescent melt of commercial purity aluminium, at various temperatures, exposed to ambient air.

Figure 2: (left) Typical transmission electron micrograph of aluminium oxide film (scale bar = 200 nm); (right) typical electron diffraction pattern.

References

Process Modelling and Integration in Developing Sustainable Metals Extraction Technologies

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Keywords: process modelling, process integration, metallurgy

Introduction

A defining feature of the metals production industry at the beginning of the 21st century is the transition to alternative sustainable technologies. In addition to the traditional imperatives like technical integrity and economic viability, a modern process design must address issues of environmental sustainability and social acceptance.

One definition of environmental sustainability [1] reads: “Producing more utility per unit throughput through the economy by maintaining the capacity of the ecosystem to sustain the physical flows and at the same time improve the public health and quality of human development.” Sustainable development in the context of metal extracting technologies has four main attributes:

1. High process efficiency
2. Full utilisation of the natural resources
3. Reliance on renewable
4. No negative impact on “human development” [2]

In order to address the complex range of economic, environmental, social and governance issues, future process development will require a broader multidisciplinary approach. Process integration is viewed as a potentially useful methodology capable of optimising complex industrial systems across the overall value-adding chain.

Process Integration

Process integration is an approach to optimise energy and material flows across a processing or manufacturing system. While utilising fundamentally similar mathematical and engineering principles, the tools employed in various industrial systems are quite diverse. The “Pinch Analysis” technique, developed by Bodo Linhoff [3,4] is often quoted as an early example of a process integration methodology. As a tool for energy optimisation it has been widely applied in petrochemical industry.

The development and implementation of process integration models and methodologies in metallurgical practice is relatively new and largely limited to iron and steelmaking processes [5-7].
In its potential ability to optimise a process across the entire manufacturing chain and broad range of parameters, the process integration methodology can play an important role in areas such as:

- Process optimisation
- Impact quantification
- Decision and policy making
- Education

Process integration is multi-disciplinary by definition and it is natural that the tools it utilises reflect that. It is in this regard that the development of this methodology requires cooperation between parties with various expertise.

Process Modelling Tools

Depending on its objectives, process design may employ a rather diverse set of modelling tools. They generally fall in the following categories:

- Process flow sheet models
- Thermodynamic models
- LCA models
- Economic models
- Kinetic and CFD models
- Optimisation routines

A number of proprietary packages in each individual category have been developed which allow analysis of a broad range of metallurgical systems. For example process flowsheet packages like Metsim [8], Aspen Plus [9], SysCAD[10] and IDEAS [11] have been applied in the minerals processing and metallurgical practice. FactSage [12], MPE [13] and Thermo-Calc [14] are examples of well accepted thermodynamic solution modelling packages in pyrometallurgy. Although LCA methodology and databases have been developed to a lesser degree, a lot of work has gone into improving their suitability for numerous geographical regions and packages like SimaPro[15] and Gabi[16] have become more widely used.

There are, however, a number of compatibility issues that hinder the integration of these tools in a comprehensive model often needed by the metallurgical engineer to address complex optimisation problems. Among these issues are database, convergence algorithms and development platform incompatibilities which are difficult and costly to reconcile. Furthermore, while the solution thermodynamic databases developed for iron and steel-making applications are fairly comprehensive, this certainly is not the case for complex non-ferrous systems. The solution thermodynamic models for aqueous systems are also far less developed than the solution models for molten slags, salts, mattes and metals.

An example of a complex integration and innovation problem is the development of alternative sustainable nickel extraction technologies from laterites where hydro- and pyrometallurgical unit operations can be incorporated in the same process flowsheet. CSIRO has undertaken the development of technologies which have the potential to reduce the energy consumption and greenhouse gas emissions in nickel laterite smelters. Dry Slag Granulation (DSG) [17] and “Design Char from Biomass”[18] are examples of such technologies. Retrofitting technologies of this kind into existing operations is an important
and challenging task considering the specificity of each plant layout, raw materials, nature of the material flows and regional market conditions.

Furthermore CSIRO has engaged in the development of detailed LCA-coupled flowsheet models of nickel laterite processing options aimed at development of technologies capable of significant reduction in energy consumption, greenhouse gas emissions, waste generation and operating cost. Another important objective is to utilise as fully as possible the laterite deposit, which is a major challenge due to its stratified nature and the lack of a single technology capable of processing the limonite and saprolite layers of the ore body. In our effort to develop these technologies and solution models we have gained some insights into the limitations and potential for development of a number of modelling tools, which might be of value to share with our colleagues in industry and academia.

Academic research has played a major role in the development of many of the modelling tools used today in metallurgical process design and integration. It has made a particularly significant contribution to the development of thermodynamic solution modelling. However there is a need for LCA development in order for it to find broad application to primary metallurgy.

The process integration toolbox for primary metals extraction is far from complete and its future development will most definitely require the consolidated effort of academia, proprietary software developers and industry. It is inspiring to see the academic research taking a leading role in this new and exciting area.

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**Powder Metallurgy: A Promising Route for Bone Implants Fabrication**

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**Keywords:** titanium alloys, alloying elements, powder metallurgy, space-holder

**Introduction**

One of the major bone tissue engineering challenges is producing biocompatible and biomechanical compatible implants which are similar to bone structures. Titanium and titanium alloys are widely used as implants due to their high corrosion resistance, excellent strength and light weight. However, the dense titanium and titanium alloys are prone to lead into aseptic loosening. The elastic modulus of dense Ti alloys is in the range of 55-110 GPa which is significantly higher than that of natural bone (0.1-30 GPa) [1]. Usually there are two ways to lower the elastic modulus, one is to produce a porous structure of the metallic alloy by adjusting its porosity, and the other is to introduce \(\beta\)-alloying element. The porous structure allows bone to grow into the pores and lock the artificial implant for better fixation, and thus mimicking the natural bone structures.

Conventional (*e.g.* sintering-pressing) and advanced (*e.g.* hot isostatic pressing) powder metallurgy (PM) has been an alternative route in producing biomedical implants. In recent years, the space holder sintering method has been widely used to produce porous titanium alloys. The basic principle of this method is to sinter both metallic powder and space holder material, *e.g.*, ammonium hydrogen, via a two-step heat treatment followed by cold pressing [2]. Compared to other techniques (*e.g.*, slurry sintering, self-propagating high temperature synthesis, and rapid prototyping), this method has been proven to produce a porous structure with flexibility to choose the desired porosity by adjusting the weight of space holder particle.

**Processing**

![Schematic process of space-holder sintering technique](image)

**Figure 1:** Schematic process of space-holder sintering technique
Firstly each component (i.e. titanium, niobium, and tin, etc.) was weighed to give a desired composition of titanium alloys. Ammonium hydrogen carbonate (NH₄HCO₃) was used as a space holder material. These components were mixed and blended in a planetary ball milling. This mixture was pressed into green compacts. The heat treatment process was conducted in two steps in a vacuum furnace. The first step was to burn out the space holder material in the green compacts at 175 °C for 2 hours, and the second step was to heat to 1200 °C and keep at this temperature for 5 hours.

Mechanical properties

Pore size and porosity is the major concern in producing porous scaffolds as it influences the mechanical properties of an implant, such as elastic moduli, mechanical strength and also the biological performance of the implant material. Porosity will enhance interlocking process for stability, and immobility of the new implant. Porosity is influenced by several factors, namely the particle size of metallic powder and sintering pressure. Reducing the particle size will reduce the porosity due to an increased surface energy per unit volume. Small diameter particle with high specific surface area have higher energy, thus sintering process of the particles will be more rapid [3]. In the sintering process, raising the pressure will decrease the porosity, as it is caused by plastic deformation of Ti powder at contact area. In addition, particle size also influences the surface energy. Chen et al. reported that by reducing the Ti particle powder size the surface energy increased, and subsequently higher surface energy leads to higher apatite inducing ability [3]. The porosity of the samples ranges from 60% to 70%. Studies revealed that the optimum porosity of the implant for bone in-growth is in the range 40-70%.

Many studies of porous Ti alloys using space-holder method showed a combination of both macropores and micropores on the cell wall. The macro-pores were mainly dependant on the size of the space holders, while the micro-pores were primarily determined by the size of the titanium powder particles. The macropore size ranges from 100 to 600 μm.

Figure 2: Morphology of porous Ti14Nb4Sn alloys with different porosities: 60% (a), and 70% (b)

It is also noted that the development of porous titanium alloys with variety of alloy components has brought many improvements in bio-mechanical properties. Production of porous Ti10Nb10Zr with 69% porosity exhibited a mechanical strength of 67 MPa, compared to 53 MPa and 35.2 MPa for pure Ti and pure Ta scaffolds with the same porosity [4]. Hence, mechanical properties could be tailored to mimic the natural bone properties.
Conclusion

Powder metallurgy by space-holder sintering method is a promising method in biomedical implant fabrication. It produces porous structure for better fixation, lowering the elastic modulus, and mimicking the natural bone structures for long life implants. The SEM results showed both micro-pre and macro-pore structures with porosities ranging from 60-70%.

References

Functionalisation of Nitride Whiskers: Synthesis, Underlying Mechanism and Potential Applications as Membrane Filters

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**Keywords:** Nitride whiskers, synthesis, mechanism, membrane filters

In order to cope with recent environmental issues with car exhaust gas and the like, there has been an increasing demand for a kind of material usable as a variety of filters, catalyst carriers and structural materials having a high heat resistance, high strength and thermal shock resistance. Compared with oxide ceramic which have been extensively used as membrane filters, nitride ceramics have aroused great interests of the researchers due to their excellent mechanical properties, good corrosion resistance and oxidation resistance etc. In recent work, it has been found that nitride ceramics can be developed into elongated whiskers which possess a high porosity up to 70% and result in much higher permeability in filtration than oxide ceramics. This makes nitride whiskers show great potential in many high-tech areas such as bio ceramics, catalyst supports and sensors, especially in severe conditions such as furnace insulators, hot-gas filters, molten metal filters and membrane reactors.

Since better performance is required in many industrial applications, the fabrication process of nitride whiskers must be carefully controlled to get proper size and microstructure etc. to meet different requirements of each particular application. However the information on synthesis of nitride whiskers with controlled morphology is very limited. One of the important factors hindering further commercial development of nitride whiskers is the materials themselves, which still need optimization and new developments. Underlying mechanism including thermodynamics and kinetics that cause the uniform structure growth of the nitride ceramics are not fully understood. In addition, their properties including oxidation resistance and mechanical properties as membrane fillers are very limited. These constrain their practical application greatly. This work aims to provide a useful guidance for the design and application of nitride whiskers. The key concept of the research is to investigate the dependence of controllable synthesis on raw materials, atmosphere and reaction temperature concerning both the related experimental data and thermodynamic calculation. In addition, their application as hot gases filter is also investigated.

**(1) Nitride whiskers synthesis and underlying mechanism**

The synthesis of nitride whiskers is a process involving both thermodynamics and kinetics. From reaction kinetics viewpoint, it is well known that the morphology of whiskers is sensitive to many factors such as the ratio of the starting composition, atmosphere and reaction temperature (as shown in Figure 1). The dependence on these factors can be explained from thermodynamic aspect. In view of $\beta$-SiAlON whiskers synthesis, two systems, Si-O-N and Al-O-N are involved during the formation of $\beta$-SiAlON whiskers from thermodynamic calculation. The equilibrium partial pressures of gases involved during the reactions are shown in Figure 2. This indicates that Al and SiO may be important
intermediate reactants during the synthesis of β-SiAlON whiskers \(^3\). Since the reaction was carried out in flowing nitrogen atmosphere, the flow rate of nitrogen was slowed down at 1773K to enable β-SiAlON whiskers to grow in a stable way (as shown in Figure 3).

![Microstructure of the synthesized β-SiAlON(z=1.6) (1700K)(a) and AlN whiskers(1873K) (b)](image)

Figure 1: Microstructure of the synthesized β-SiAlON(z=1.6) (1700K)(a) and AlN whiskers(1873K) (b) \(^{1,2}\)

![Equilibrium partial pressure of gases in Si-O-N system (a) and Al-O-N system (b) at 1800K](image)

Figure 2: Equilibrium partial pressure of gases in Si-O-N system (a) and Al-O-N system (b) at 1800K

![FESEM photographs of β-SiAlON (z=1.6) whiskers synthesized at 1773K for 6h](image)

Figure 3: FESEM photographs of β-SiAlON (z=1.6) whiskers synthesized at 1773K for 6h
(2) Properties of nitride whiskers-oxidation resistance

Considering the possible application of nitride whiskers as hot-gas filters that are possibly applied under high temperature and oxygen containing atmosphere, the oxidation resistance of nitride whiskers should be investigated. The recent investigations show that the oxidation behaviour of AlN wishers is quite different from that in the form of powder or pellet because of the effect of shape\(^1\).\(^4\).

In order to evaluate the oxidation resistance of materials, many models have been proposed by researchers in the literatures, such as the well known Jander’s equation, the parabolic rate law and the linear rate law. These models were developed based on gas-solid reaction and usually expressed with a pre-exponential term \(k\) and an apparent enthalpy. However, the constant \(k\) does not have clear physical meaning and thus these expressions are only empirical fits and used for interpolating the available data. In addition, the current models used in the literatures are established on the following assumption, i.e. \(\frac{d\xi}{dt} = k \xi^{-\frac{T}{T^*}}\), where \(f(\xi)\) is a function of reacted fraction \(\xi\) (some researcher called it as the reaction model) and \(k(\xi)^*\) a function of temperature \(T\), normally it can be expressed as an Arrhenius equation, \(k(\xi) = A \exp\left(-\frac{\Delta E}{RT}\right)\). Apparently, the form of \(k(\xi)\) means that the variables \(\xi\) and \(T\) can be expressed separately in an expression, which actually is an important assumption for these models. Therefore, the applicability of these models depends on the reliability of this assumption. In general, this assumption might be acceptable. However, big errors will be introduced under the conditions that the reaction is controlled by multiple steps or the shape of the sample is other than a sphere. In the authors’ own work\(^5\), Chou’s model has been developed, in which the mass change is expressed as a function of various factors. The new model has been developed based on some approximate but reasonable assumption. It is different from all current models available in the literatures because it is established on a real physical picture with certain size or shape of solid materials undergoing a real process of molecular and atom movement. Using this new model, one can perform a calculation easily and give a good theoretical discussion for practical problem\(^4\).

![Figure 4: A comparison of experimental data with model for isothermal oxidation curves at 1423K](image)

**Figure 4:** A comparison of experimental data with model for isothermal oxidation curves at 1423K.
References

Phase Equilibria Studies in the System “FeO”-SiO$_2$-CaO-Al$_2$O$_3$-MgO under Controlled Oxygen Partial Pressures

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**Key words:** copper smelting, copper converting, liquidus temperature, slag

One of the important objectives of copper smelting/converting process is to remove impurities from matte or metal through the formation of the slag phase. The major components of the copper smelting and converting slags are iron oxide and silica. Other components can also present in the slags, such as CaO, Al$_2$O$_3$ and MgO. Knowledge of the phase equilibria information of this slag system “FeO”-SiO$_2$-CaO-Al$_2$O$_3$-MgO is required to determine the optimum operating temperature. Phase equilibria of ferrous silicate slags in the systems “FeO”-SiO$_2$-CaO-Al$_2$O$_3$ $^1$ and “FeO”-SiO$_2$-CaO-MgO $^2$ at iron saturation have been investigated in the composition ranges related to copper smelting slags. However, they are not sufficient to accurately describe the commercial copper smelting/converting processes that operate at intermediate oxygen partial pressures $10^{-5}$ to $10^{-9}$ atm. Limited information is available at these specific conditions.

The experimental procedures developed at the Pyrometallurgy Research Centre (PYROSEARCH) that have been used, include equilibration of synthetic slag at high temperatures and controlled P$_{O_2}$, rapid quenching of resulting phases, and accurate measurement of phase compositions using electron probe X-ray microanalysis (EPMA) $^{1-3}$. The effects of CaO, Al$_2$O$_3$ and MgO on the phase equilibria of this slag system have been experimentally investigated in the temperature range 1200 to 1300 ºC and oxygen partial pressures between $10^{-5}$ and $10^{-9}$ atm.

It was found that spinel and tridymite are major primary phases in the composition range related to copper smelting/converting slags. In addition, wustite, olivine, diopside and pyroxene may also appear at certain conditions. Typical microstructures of the quenched samples are presented in Figure 1, showing well-quenched liquid slag in equilibrium with spinel (Figure 1a) and tridymite (Figure 1b) respectively.

The presence of CaO, MgO and Al$_2$O$_3$ in the slag was found to increase liquidus temperatures in the spinel primary phase field and decrease liquidus temperatures in the tridymite primary phase field. Liquidus temperatures in the tridymite primary phase field are not sensitive to P$_{O_2}$; liquidus temperatures in the spinel primary phase field increase with increasing P$_{O_2}$. Liquidus temperatures in the tridymite primary phase field decrease with increasing “FeO”/SiO$_2$ ratio and liquidus temperatures in the spinel primary phase field increase with increasing “FeO”/SiO$_2$ ratio.
Phase diagrams in the multi-component systems “FeO”-SiO$_2$-CaO-MgO-Al$_2$O$_3$ for convenience of use are often presented in a form of pseudo-ternary sections “FeO”-SiO$_2$-CaO at fixed Al$_2$O$_3$ or MgO concentrations. For these multi-component systems it is difficult to experimentally obtain the exact target concentrations of all components in the liquid phase (for example, MgO = 4.0 wt %) due to the precipitation of solid phases from the melt and interaction of the liquid with the container/substrate. An optimisation procedure is therefore introduced for all experimental data having a range of concentrations of the minor components Al$_2$O$_3$ or MgO in the liquid at a given primary phase field, temperature and oxygen partial pressure. The basis of the optimization is that at a given CaO concentration in liquid the “FeO”/SiO$_2$ ratio in liquid is function of Al$_2$O$_3$ and MgO concentrations. The experimental measurements can then be described by the following empirical equations:

\[
X(F/S) = \frac{F_0 + F_{Ca1}*(X_{Ca})^2 + F_{Ca2}*(X_{Ca} + F_{Al}X_{Al} + F_{Mg}X_{Mg}}{1(1+X(F/S))}
\]

\[
X_{Si} = \frac{100-X_{Ca} - X_{Al} - X_{Mg}}{1+X(F/S)}
\]

\[
X_{Fe} = X_{Ca} - X_{Al} - X_{Mg} - X_{Si}
\]

where X(F/S) is weight ratio of “FeO”/SiO$_2$, $F_0$, $F_{Ca1}$, $F_{Ca2}$, $F_{Al}$ and $F_{Mg}$ are interpolation coefficients obtained for a given temperature and Po$_2$ by minimising the sum of squared differences of experimental and calculated concentrations, and $X_{Si}$, $X_{Fe}$, $X_{Ca}$, $X_{Al}$ and $X_{Mg}$ are concentrations of SiO$_2$, “FeO”, CaO, Al$_2$O$_3$ and MgO respectively in weight percent present in the liquid phase at the liquidus.

The examples of the interpolation results for relationships between “FeO”/SiO$_2$ ratio and MgO or CaO in liquid are shown in Figure 2 for 1200 °C and Po$_2$ = 10$^{-8}$ atm for the spinel primary phase field. It can be seen that both MgO and CaO have significant effects on the “FeO”/SiO$_2$ ratio in the liquid. It can be seen from Figure 2a that at a given CaO concentration the “FeO”/SiO$_2$ ratio in the liquid decrease with increasing MgO concentration. The slopes of the three lines in Figure 2a are approximately -0.031 regardless CaO concentrations. That indicates that increase of 1 wt% MgO in the liquid requires decrease of “FeO”/SiO$_2$ weight ratio by 0.031 to ensure the liquidus temperature to be 1200 °C at Po$_2$ = 10$^{-8}$ atm. Similarly, Figure 2b shows that at a given MgO concentration the “FeO”/SiO$_2$ ratio in the liquid decrease with increasing CaO concentration. However, the relationship between “FeO”/SiO$_2$ ratio and CaO is not linear. “FeO”/SiO$_2$ (or Fe/SiO$_2$) ratio is commonly used in industrial operations to control the slag composition. The results shown in Figure 2 can be
used by copper smelter to adjust the “FeO”/SiO₂ weight ratio according to the CaO and MgO concentrations in the slag. It is well known that liquidus temperatures in spinel primary phase field increase with increasing “FeO”/SiO₂ ratio. Increased CaO and MgO concentrations in the slag require extra SiO₂ flux to avoid the formation of spinel solid.

Figure 2: Correlations between “FeO”/SiO₂ ratio and a) MgO and b) CaO concentration in the liquid in equilibrium with the spinel at 1200 °C and P O₂ = 10⁻⁸ atm. The number above each of the symbol is the actual CaO or MgO concentration. Solid symbols: experimental results; Open symbols: interpolated points; Straight line: best fitted line for the given CaO or MgO concentration

Acknowledgement
The authors would like to thank Ms Jie Yu for general laboratory assistance and careful sample preparation, The Australian Research Council Linkage program, BHP Billiton Olympic Dam Operations, Rio Tinto Kennecott Utah Copper Corporation, Outotec Oy, Xstrata Copper and Xstrata Technology for their financial support for the project.

References
Use of CFD and Physical Experimentation to Understanding Slag Droplet Behaviour and Formation from a Spinning Disc

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1CSIRO MDU Flagship

Keywords: CFD Modelling, Dry Slag Granulation, Droplet breakup, free surface flows, spinning disc

Large volumes of slag are produced by metallurgical processes, such as blast furnaces for steel production, and represent a significant waste stream that with suitable processing can be used in other industrial processes. Water granulation is currently used to process much of this slag but it uses large quantities of water and does not recover any of the heat. CSIRO is developing a dry slag granulation (DSG) process (Xie and Jahanshahi, 2008) based on a spinning disc that produces glassy slag granules and recovers some of the heat contained in the slag.

The DSG process uses a spinning disc to break up a stream of molten slag into droplets that are then cooled by air and contact with the vessel walls. CFD modelling using ANSYS/CFX has been undertaken to develop an understanding of the slag film behaviour on the spinning disc (Pan et al. 2010) and the droplet formation process (Pan et al. 2011). A number of experiments have also been performed to understand the way that droplets interact with the vessel’s walls so that information on droplet rebound and heat transfer can be determined and subsequently implemented into a CFD model of the process.

Key parameters to stable operation of the disc are control of slag flow across the disc, limiting disc temperature and formation of a solid frozen slag on the surface of the disc. To understand disc operation a CFD model of disc that accounts for formation of a solid frozen slag layer at the disc surface and spreading and formation of a liquid slag film on the disc was developed. Results from the model of the temperature distribution in the air, slag and disc as well as the predicted slag film thickness on the disc are shown in Figure 4.

A model has also been developed that predicts the breakup of the continuous slag film as it leaves the disc, the first stage is the formation of ligaments that then break into droplets. The model is a transient VOF based simulation and results showing the typical breakup behaviour are shown in Figure 5.

This paper reports on progress made in developing CFD models of the disc and droplet formation process. A summary of some of the key fundamental experimental work performed to understand the interaction of droplets with walls will also be presented.
Figure 4: Predicted temperature (left) and liquid slag free surface profile (right).

Figure 5: Predicted droplet formation from a spinning disc. (Disc type: A, Liquid slag tapping rate: 5 kg.min\(^{-1}\), Disc spinning speed: 2000 RPM, Time: 30 ms)

References

Decarburization of Steel under Inert Condition

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**Keywords:** decarburization, molten steel, steelmaking, argon

A horizontal tube furnace was used to study a decarburization of steel (i.e. carbonyl iron) containing 99.8 wt. % iron (Fe) and 0.007 wt. % carbon (C) at 1600°C and under argon (Ar) atmosphere. The inert condition was applied throughout the experiment to control reactions of the melt and avoid any contamination. Off-gases (i.e. carbon monoxide (CO) and carbon dioxide (CO₂) ) was analysed on-line by using an infrared (IR) gas analyser, while LECO® analysed initial and final C content in metal. The literature and this work results showed that CO₂ generation is very low compared to CO one. Therefore, CO generation has been considered for representing the removal of carbon. The proposed mechanism for decarburizing steel under inert condition was worked and low levels of carbon have been achieved successfully (i.e. 58ppm).

The experimental setup is as shown in figure 1. The internal diameter of alumina tube is 50 mm. The heating elements used are manufactured by Super-Kanthal. The furnace involves two zones. The 1st one is the cold zone that is for preheating the sample and holders before the followed zone (i.e. the hot zone) and for cooling them after as well. The 2nd one is the hot zone for melting the sample. The preheating and cooling steps are made to avoid thermal shock. During the melting experiment, a video camera was used to monitor melting, gas evolution, and stabilisation.

![Diagram of experimental setup](image)

**Figure 1:** Schematic of the experiential arrangement using the horizontal tube furnace (Yunes & Sahajwalla 2009)
To avoid dust formation and better conductivity during the experiments, the iron powder was converted into 10g size pellets by hydraulic pressing machine as a preparation for the experiment. The pelletized sample was placed in a ceramic crucible standing on a holder that transported the crucible inside the furnace.

The following reactions are assumed to occur during decarburization experiment according to material contents and thermodynamics calculations:

\[
\begin{align*}
[C] + [O] & = \text{CO}_{(g)} \quad \Delta G = -94 \text{ kJ mol}^{-1} \quad \text{(Kawai & Mori 1988)} \\
[O] + [O] & = \text{O}_2(g) \quad \Delta G = -444 \text{ kJ mol}^{-1} \quad \text{(FactSage™ 6.2 2010)} \\
[C] + \frac{1}{2}\text{O}_2(g) & = \text{CO}_{(g)} \quad \Delta G = -275 \text{ kJ mol}^{-1} \quad \text{(Turkdogan 1980, 1993 & 1996)} \\
[C] + \text{FeO} & = \text{Fe} + \text{CO}_{(g)} \quad \Delta G = -127 \text{ kJ mol}^{-1} \quad \text{(FactSage™ 6.2 2010)}
\end{align*}
\]

Furthermore, a qualitative analyses have been practiced to monitor sample developments during the experiment. The CO generation has been observed by the video system during the processing time as seen in figure 2. On the other hand, the parametric analysis showed the carbon reduction on-line by using the IR gas analyser and by analysing the initial and final carbon content in the solid phase. As seen in figure 3.

![Figure 2: Illustration of CO generation and sample developments throughout the experiment.](image)

![Figure 3: Illustration of carbon removal throughout the treatment.](image)
In conclusion, the proposed methodology has been tested successfully in light of
thermodynamics, quantitative and parametric analyses. Therefore, the promising result was
the driving force to proceed the study of the decarburization of steel in different conditions.
Further investigations and experimental works are going to be presented in the next HTP
upcoming occasions.

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Marangoni Instabilities in Single Droplet Extraction Systems

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Keywords: Marangoni convection, liquid/liquid extraction, single droplet, CFD modelling

Single droplets immersed in an ambient liquid represent the smallest transfer unit in a liquid/liquid system. Dispersed multiphase extractive systems occur in many industrial processes. Conventional applications in chemical, oil or high temperature processes in metallurgical industries are more and more supplemented by applications in the food and pharmaceutical industries, biotechnology and environmental engineering.

The transport phenomena in these polydispersed systems are linked in a highly complex manner via the properties of the droplet interface. Thus, the understanding of interfacial phenomena in extractive liquid/liquid systems is essential for the phenomenological and theoretical description of solute mass transfer across the interface of droplets. In particular the Marangoni convection has potential to substantially increase the interfacial molar flux, i.e. the mass transfer coefficient\(^1,2\) and impacts in a highly complex manner the fluid dynamics of the system, provided the interface is free from contaminants and surfactants.\(^2\) However, in industrial applications, surfactants can hardly be avoided (or they are essential for the process). These surfactants can significantly affect the mobility of the interface, and on the other hand, due to their ability to lower locally the interfacial tension, they can initiate Marangoni effects and thus additional interfacial convections.\(^3\)

The Marangoni convection occurs at interfaces with significant interfacial tension gradients, originated from differences in interfacial solute concentration, temperature or electrocapillary potential. The system tends to minimize its surface energy and expands regions of lower towards regions of higher interfacial tension \(\sigma\) (see Figure 1). This process will generate a tangential interfacial convection which leads to - in cases of small damping – chaotic flow patterns within the droplet. These flow patterns promote inner radial mixing and thus transfer of matter.

Whenever Marangoni convection occurs, there is a two-way coupling between concentration and flow field which makes the whole process complicated. Despite many research activities on this field, a complete physical understanding is still missing, and modelling attempts did not lead to satisfying and reliable results.

In the work presented here, detailed experimental investigations of the impact of Marangoni convection on mass transfer and fluid dynamics at single droplets have been carried out in a well-proven test extraction column\(^2,4\) supported by the development of a fully 3D CFD
model. The ternary system toluene/acetone/water is used which is known to show mass transfer enhancement due to Marangoni convection. In the experiments, toluene is the dispersed phase and water is the continuous phase. The mass transfer direction of the solute acetone is directed from the dispersed to the continuous phase \((d \rightarrow c)\). The varied parameter is the initial solute concentration and the droplet diameter. Acetone laden toluene droplets with a desired diameter are formed at a nozzle using a precision dosing pump and released by a solenoid device. They rise in the quiescent toluene saturated water phase until they are collected by a funnel device at desired contact times. The mean acetone concentration in the droplets is analysed using gas chromatography.

For the simulations, the commercial Finite Volume package Star-CD v. 3.24 (cd-adapco) has been used. A fully 360° model (thus no symmetry planes) of a droplet in an ambient phase has been conceived. The Marangoni convection has been implemented by using user defined subfunctions which allow modification of the shear stress boundary condition. Transient simulations of spherical droplets in a moving reference coordinate system have been performed, and the mean concentration of the solute has been calculated as a function of time, and compared with experimental data. To the author’s knowledge, this is for the first time that 3D numerical simulations of Marangoni convection in single droplets have been conducted and validated with experimental data.\(^5\)

Figure 2 shows the mean solute concentration as a function of time for a 2 mm toluene droplet for different initial solute concentrations. The enveloping simulation curves give the boundaries indicating perfect mixing (no internal resistance to mass transfer) and constant interfacial tension (no Marangoni convection). The experimental data for 1.8 and 30 g/L lie in between these two curves. The higher the initial solute concentration is, the more Marangoni instabilities are promoted. The enhancement factor of mass transfer is between 2-3, i.e. mass

![Figure 2: Relative mean solute concentration in 2 mm toluene droplets as a function of time for different initial solute concentrations. Curves: numerical results, symbols: experimental data.](image-url)
transfer is 2-3 times faster in the case with Marangoni convection compared to the case of constant interfacial tension. The simulations are in good agreement with experimental data and reflect the physics of the system dominated by Marangoni effects.

Figure 3 shows $t_{50}$ and $t_{60}$, the times at which 50% and 60% respectively of the mass transfer has been completed (initial solute concentration $c_{A0} = 30$ g/L, mass transfer direction (d→c), as a function of droplet diameter. Again, numerical results are compared to experimental data. The larger the droplets are, the more time is needed to transfer the solute to the interface. In the spherical droplet regime, excellent agreement between experiments and simulations has been observed. The situation changes in the oscillating regime where a distinct break in the curve occurs. The CFD model fails to predict $t_{50}$ and $t_{60}$, since it only accounts for spherical droplets in clean systems. Thus, subsequent studies comprised the effect of droplet oscillation and surfactants in Marangoni dominated systems. Currently, on the numerical side, a front-tracking model is being developed by our collaborators at the University Erlangen-Nuremberg, Germany, to account for the impact of Marangoni convection in deformable droplets with and without surfactants.

![Mass transfer times $t_{50}$ and $t_{60}$ as a function of droplet diameter. Comparison of experimental and numerical data.](image)

**Figure 3**

**References**

EAF Scrap Preheating Technologies

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Electric steelmaking accounts for approximately 35% of the world steel production. In the past two decades, the increase in the proportion of steel made by Mini Mills (Electric Arc Furnace based steelmaking) has been remarkable in North America, Europe and South-East Asia.

Over 50% of the energy used to produce rebar in Mini Mills is electric energy used at the EAF.

![Energy Use in Mini Mill Factory](image1)

Off-gas energy losses account for about 22% of an EAF energy balance (approximately 55% of total energy losses).

![Energy Flow Diagram](image2)
The energy recovery potential of the EAF process is high; various technical solutions were devised in the last 40 years in order to utilise off-gas heat to preheat the steel scrap.

The increase in energy cost (electrical energy and in particular fossil energy – Carbon Tax) and the increasing raw material cost are demanding actions from steel makers and furnace designers to be able to optimise the conversion cost of the melting operation and increase the productivity of the EAF to gain a competitive edge.

In this context, scrap preheating can be helpful in reducing the overall EAF energy consumption. Assuming an average preheating temperature between 400 and 600°C and an overall melting efficiency between 70 and 80%, energy savings between 80 and 120 kWh per tonne of liquid steel are possible.

![Scrap Preheating Effect](image)

Scrap preheating technologies pursue the following goals:

- To Reduce:
  - Total Energy Consumption
  - Electrode consumption
  - Refractory consumption
  - Power on and tap to tap time
  - Conversion cost
  - CO₂ Emissions

- To Increase:
  - EAF Productivity

The following technologies are nowadays available in the market to respond to these requirements:

- Bucket Scrap Preheating Systems (Daido, NKK, Krupp, SMS-Demag, Siemens-VAI, Danieli)
- Rotary Kiln Preheater (BBS-Brusa)
- Shaft Furnaces – Single, Double and Finger Shafts (Siemens-VAI)
- EcoArc Shaft Furnace (NKK)
- Shaft Furnace with pusher (IHI)
- COSS Shaft Furnace (Fuchs)
- Continuous scrap preheating systems (Tenova Consteel Process, Danieli ESC System)
- Twin Shell Furnace
- Single Bucket High Shell Furnace
**Why Do We Need New Inclusion Experimental Techniques?**

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**Key words:** inclusion additions, morphology, formation, secondary steelmaking

There is an ever increasing demand for cleaner steels, that is, those with low oxide inclusion content. This demand has highlighted the limitations of our current knowledge in controlling and predicting inclusion development during liquid steel processing.¹ The formation of inclusions during liquid steel refining is an unavoidable consequence of the current industrial steelmaking process. Steel leaving a steelmaking converter contains anything from 400-1000 ppm of oxygen in solution [O].² The [O] concentration needs to be reduced to less than 30 ppm to be cast. If not, it will react on solidification producing gas and condensed oxides. If cast in such a condition the steel would be virtually worthless, containing significant porosity and oxide matter resulting in extremely poor mechanical properties.

To lower the [O] to a level so that the steel can be cast, the [O] is reacted with elements/compounds that have a strong affinity with oxygen, such as Al, Ca and Si. These are deoxidants and the process is referred to as deoxidation. The resulting oxides (inclusions) would then ideally be removed from the liquid steel by stirring it to promote particle reaction with a slag phase. Further, there are additions or steel processing specifically intended to modify the inclusions, either to enable their removal or to achieve a particular phase/morphology required for casting. In steel refining a classic example of particle modification would be Ca injection into the melt to modify solid Al₂O₃ inclusions formed by Al deoxidation. The Ca reacts with solid Al₂O₃ forming a liquid calcium aluminate that is easier to remove to the slag, less detrimental to the physical properties of the solidified steel and can also confer some local refining benefit by tying up [S] prior to casting.³

Key knowledge gaps in this area are primarily a result of the complex nature of the problem. There is uncertainty with respect to the changes in phase and morphology of the inclusions with steel processing. In particular, there are difficulties predicting when an inclusion is liquid for a given set of conditions. To some extent this is due to the fact that industrial steel melts often are used in the inclusion studies. This is true whether these are on an industrial scale or simply the steel used in the laboratory experiments.¹,³⁻⁶ There are other issues relating to classical metallography and SEM analysis techniques for inclusions in steel and laboratory scale experiments.

Industrial steel melts have a complex chemistry and potentially a complex array of inclusion types. This can often obfuscate any cause and effect analysis with respect to the refining process. Further, particularly on full scale industrial processing studies, the melt composition is often necessarily transient. For example, it can be expected that soluble calcium [Ca] is lost from the steel melt during vacuum degassing to remove hydrogen or carbon as CO gas and to
stir the melt to promote inclusion removal to the slag phase. The Ca oxide based or Ca sulphide based inclusions will be reduced to replace this lost [Ca] and thereby modify the inclusions.\textsuperscript{3, 4} Under such circumstances it is difficult to separate out the modifying effect of the change in steel melt composition on inclusion reactivity/removal to the slag and the stirring effects to promote slag-steel contact on inclusion removal. Thus, loss of [Ca] and resultant inclusion modification in industrial melts results in unwanted inclusions such as CaO.2Al\textsubscript{2}O\textsubscript{3} and CaO.6Al\textsubscript{2}O\textsubscript{3} that can cause rapid clogging of pouring tubes and reversion of S to the melt.

The transient nature of the melt can also result from steel-slag or steel-refractory interactions. For example in Al deoxidised steel the aluminium in solution [Al] can reduce MgO in the slag or refractory to magnesium in solution in the steel [Mg]. Once in the steel this [Mg] is able to react with the Al\textsubscript{2}O\textsubscript{3} inclusions to form a spinel (MgAl\textsubscript{2}O\textsubscript{4}).\textsuperscript{4, 6} Other mechanisms have been proposed for how the Mg enters solution from the refractories. Jansson et al\textsuperscript{7} studied the reactions of carbon bonded MgO and Al deoxidised steel and proposed that Mg vapour formed via carbon reduction of the MgO and it was this vapour that reacted to form [Mg]. Spinel formation is generally considered a problem causing clogging of pouring tubes, limiting productivity and poor surface quality of final product due to the high hardness of the spinel. It is important to fully understand how and when this may form and how it could be modified to aid its removal to the slag phase.

Classical metallography and SEM analysis techniques for inclusions in steel have been widely used to analyse the morphology and composition of inclusions in liquid steel. Even though these techniques have provided significant information, it is qualitative and time consuming. In addition to being time consuming, the small area of the sample analysed raises questions about how representative the analysis is.\textsuperscript{1, 5, 6} The number of inclusions being reported is usually low, particularly in clean steels. Recent studies by the authors\textsuperscript{8} and others\textsuperscript{9} have shown that there is segregation with respect to inclusion content in the standard steel button sampling techniques used in industry. This is also likely to be true of samples from laboratory experiments but the authors do not know of any reported work discussing this issue. It should be noted that the representative issues raised above relate to analysis of the sample. The SEM technique has become automated that is able to detect large numbers of inclusions (>5000) and assess with respect to size and composition, inclusions in steel. The ASPEx\textsuperscript{TM} and ESPRIT Steel\textsuperscript{TM} SEM automatic inclusion analysis techniques cut down inclusion analysis times to a few hours on something that would have previously taken weeks.\textsuperscript{1, 5, 6} Judicious application of these new techniques in inclusion studies is likely to lessen the uncertainty in inclusion analysis.

Laboratory scale inclusion experiments using liquid steel are extremely difficult. There is a tendency for the crucible material (usually Al\textsubscript{2}O\textsubscript{3} or MgO) to react with the inclusions thereby cleaning the steel. The principle problem when this happens is finding any inclusions in the steel. In addition to this, the observed changes in the inclusions may be dominated by crucible reactivity. This problem can be overcome by use of levitation techniques or doping of the steel with synthetic inclusions and using one of the aforementioned automatic inclusion analysis techniques.

There have been many excellent and worthwhile works that have used synthetic steel made from high purity reagents\textsuperscript{10, 11} (as opposed to steel from the industrial processes). Generally when using this approach there is an attempt to form inclusions in-situ. Even though these studies offer better control over the steel melt compositions, control of the inclusion
formation and composition is extremely difficult. Normally synthetic inclusions are not added to a steel melt because of the difficulty in getting inclusion past the melt-gas interface and doing this without significant agglomeration of the particles.

In this study a new experimental technique has been developed to assess inclusion changes with time during processing. It involves the production and use of synthetic inclusions that are reacted in a synthetic steel melt composition, where both the inclusion and melt properties are closely controlled. It is believed that this approach will overcome the inherent reproducibility and uncertainty problems associated with the use of industrial steel melts. To add the synthetic inclusions to the steel a technique has had to be developed that overcomes problems of passage of the inclusions through the gas-melt interface and inclusion agglomeration. It involves sandwiching the particles between two steel disks at high pressure, prior to adding the particles to the steel melt. The view of steel disks before and after pressing is given in Figure 1. This solution offers research possibilities with respect to inclusion reactivity that hitherto were either problematic or impossible.

![before (~10 mm square, 6mm thick) vs after (~20 mm square, 0.2 mm thick)](image)

Figure 1: The comparison of the view of two steel disks before and after pressing

Further, in addition to the development of the experimental technique, the use of the analytical automatic SEM techniques such as ESPRIT and ASPEX will be used in characterising the experimental samples. It is believed this will address many of the issues researchers and industrialists have had regarding the representative nature of the particles and steel studied to real industrial melts. Preliminary work has focused on establishing the efficiency of the new experimental technique; specifically how effective the inclusion addition and sampling techniques were. To do this zirconia and cerium oxide were added to a steel melt as tracers, using the sandwiching technique. At this point no attempt to control the starting melt composition and steel supplied by BlueScope Steel was used. This steel contained no zirconia and cerium oxide, therefore any of these compounds found in the melt would confirm successful inclusion addition. The microanalyses of an inclusion of the industrial melt using the ESPRIT Steel technique is given in Figure 2. The initial size of the zirconia additions was 30μ but was reduced down to approximately 5μ after pressing the steel disks. In Figure 2, it can be seen that a zirconia inclusion was attached to an Al₂O₃ inclusion. It was found that the size of the zirconia inclusion was around 1μ which may be due to the break-up of the inclusion under experimental conditions or reaction with the Al₂O₃ inclusion.
Figure 2: Observation of an inclusion including zirconia in industrial melt using the ESPRIT Steel technique.

References

Innovative Use of Rubber Tyres and Plastics in EAF Steelmaking

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Keywords: Electric Arc Furnace (EAF), Rubber, Plastics

Electric Arc Furnace (EAF) steelmaking uses carbon based materials as slag foaming agents and as carburisers. Traditionally, anthracite and metallurgical coke are among the materials used as slag foaming agents and flat iron and lump cokes are used as carburising agents. With the ever strengthening requirements on the reduction of energy consumption and greenhouse gas emissions, there is a growing incentive to use alternative carbon sources, e.g. end of life rubber tyres and recycled plastics, to partially replace the conventional carbon materials.

The use of rubber tyres in EAF steelmaking for foamy slag optimisation has been studied in detail in collaboration with UNSW in laboratory testing and OneSteel has developed and commercialised an engineering system through plant trials for EAFs to inject blends of rubber from end of life tyres and coke into EAF as slag foaming agents.

The benefits of increasing the volume and foaminess of the slag include improved electrical energy efficiency due to a longer arc and improved heat transfer from the arc to the steel, as well as decreased heat loss through the slag and sidewalls. EAF steelmakers using PIT can also expect to see improvements in yield, inject oxygen consumption, refractory and electrode consumption, and injection system wear.

The Rubber Injection Technology (PIT) has become a standard process at OneSteel’s Sydney and Laverton EAF Steel Mills and has achieved significant milestones at the end of December 2012

- 40,720 heats tapped with rubber injection
- 13,721 tonnes of coke reduced due - substituted and reduction in injection due to FeO control and consistent sizing
- 1,128,486 equivalent passenger tyres used

OneSteel has also recently completed commercialisation of the PIT at UMC, Thailand and expects to commercialise PIT at many more overseas EAF plants.

OneSteel is developing an engineering technology to use composite materials from by-products such as coke fines and recycled plastics as carburisers in EAFs. Plant trials have shown potential improvement in carbon recovery efficiency. PCT has been lodged for this technology.
CFD Modelling of Shrouded Jet Impingement on a Liquid Surface

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\textbf{Keywords:} Computational fluid dynamics, Shrouded supersonic jet, Oxygen steelmaking, Penetrating cavity mode, Splashing cavity mode.

A computational fluid dynamics (CFD) model was developed to simulate the liquid flow field and surface deformation caused by an impinging shrouded supersonic jet on a liquid bath from the top as used in oxygen steelmaking. Air and water was used to simulate the gas and liquid phases respectively, inside the steelmaking furnace. No slag condition was assumed. Two different computational domains were used to avoid the difficulties that arise from the simultaneous solution of compressible gas phase and incompressible liquid phase\cite{1}. The two computational domains were: 1) single phase domain and 2) multiphase-domain. In the single phase domain, the compressible gas phase was solved and the gas–liquid interaction was simulated in the multiphase domain. The effect of shrouding gas flow rates on the axial jet velocity distribution, depth of penetration and velocity distribution of liquid phase were investigated. A high shrouding gas flow rate was found to increase the potential core length of the jet, depth of penetration and liquid free surface velocity which in turn contributes in reducing the mixing time. The results were validated against the experimental data\cite{2}. The CFD model was found to under predict the penetration depth and the possible reasons behind the under prediction were discussed. The mechanism of droplets generation, from the cavity surface, was investigated in detail. The predicted surface waves inside the cavity and consequent liquid fingers from the edge of the cavity were found to be in reasonable agreements with the previous experimental studies\cite{3, 4}. It was shown from the previous studies\cite{5} that the Blowing number theory ($N_B$) fails to predict the droplet generation rate if the cavity operates in the deep penetrating mode. The possible reasons behind this limitation have been discussed using the Blowing number equation and CFD results. Blowing number is a dimensionless number, proposed by Subagyo \textit{et al.}\cite{6} based on Kelvin-Helmholtz instability,

\[
N_B = \frac{\eta^2 \rho_g U_j^2}{2\sqrt{\sigma \rho_l}}
\]

Where $\eta = 0.44$ was used. The present CFD study showed that $\eta$ value changes with lance height and a constant value of $\eta$ cannot be used at all lance heights as shown in Figure 1. Finally, cavity surface area was found to be the most influencing factor in the generation of
Figure 1: Variation of $\eta$ value with lance heights.

liquid droplets. The higher the surface area, the more is the droplet generation rate. The cavity surface area is small when the cavity operates in deep penetrating mode. Then it increases when the cavity transforms from the penetrating to splashing mode with increasing lance height. But after a certain lance height, the momentum of the jet becomes the dominant factor. In this period, droplet generation rate decreases with increasing lance height because of the decrease in jet momentum.

References

Electrocapillary Phenomena in Molten Metal-Slag Systems

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**Keywords:** electrocapillary phenomena, interfacial tension, molten metal, molten slag, metallurgical processes

Electrocapillary phenomena are phenomena associated with the variation of the interfacial tension at the metal-electrolyte boundary caused by the change of the electric (electrode) potential of metal. These phenomena include the motion of metal-electrolyte interface driven by the electrically-induced gradient of the interfacial tension.

Molten slags consist of ions and thus they are electrolytes. The underlying physics and chemistry of the electrocapillary phenomena in high-temperature systems are in many aspects similar to those for aqueous solutions, which have been described in a number of fundamental studies [1]. The formation of the metal-electrolyte interface incorporates the formation of electric double layer (e.d.l.) at this interface [1]. Within the e.d.l. the metal surface and the adjacent electrolyte (e.g., slag) have equal but opposite electric charges. The application of an external voltage to the metal-slag interface causes variation of the charge density within the e.d.l. ($\varepsilon$), hence it alters the energy of the metal-slag interaction at the interface. Therefore, the interfacial tension ($\sigma$), which is the excess free energy of the interface, will vary. The generalised equation of electrocapillarity was derived by A. N. Frumkin [2]:

$$-d\sigma = \varepsilon \cdot d \varphi + \sum_i \Gamma_i \cdot d \mu_i ,$$  \hspace{1cm} (1)

where $\varphi$ is the electric (electrode) potential of metal, $\Gamma_i$ is adsorption (excess concentration) of a component $i$ at the interface and $\mu_i$ is the chemical potential of the component $i$.

This equation may be considered to be a variation of Gibbs’ equation of capillarity where the contribution of the electrostatic energy to the excess free energy of the interface is introduced explicitly. The equation of electrocapillarity (1) shows, that in an electrochemical system the excess free energy of the interface (the interfacial tension) depends not only on the chemical potentials of the components adsorbed at that interface, but also on their electrostatic energy. The electrode potential of metal $\varphi$ varies when the composition of the contacting phases change, but it also may be varied by an external source of electric power connected to an electrochemical system. This provides means to control the interfacial tension at the metal-slag boundary.

In high-temperature systems the application of voltage to the metal-slag interface is associated with the flow of electric current through the interface, i.e. with the occurrence of electrode processes. In a rigorous treatment, the equation of electrocapillarity can only be used for the analysis of the phenomena occurring under equilibrium conditions (i.e. with no electric current crossing the interface). However, when the flow of electric current through the metal-slag interface is associated with fully diffusion-controlled electrode processes, the application of equation (1) is still possible. This is because, in this case, the adsorption of
components at the interface will be in equilibrium with the adjacent layers of slag. In metallurgical systems this condition is often met.

In the case when the external electric field generates a non-uniform distribution of electric charge along the metal-slag interface, the interfacial tension varies along that interface. As a result the interface starts moving from the areas with lower interfacial tension towards the areas with higher tension and the so called “surface tension driven flows” arise. The convective flows accompanying the motion of the interface will accelerate the mass transfer between metal and slag and, for dispersed systems, will cause the motion of droplets of the dispersed phase.

**Experimental data on electrocapillary phenomena in metallurgical systems**

Two kinds of electrocapillary phenomena have been studied in high-temperature metallurgical systems:

(1) variation of the interfacial tension \( \sigma \) at the “metal – slag” boundary with the variation of the electrode potential of metal \( \varphi \), which can be presented graphically as an electrocapillary curve (ECC);

(2) motion of metal drops in slag under the influence of electric field applied to the slag – the electrocapillary motion (ECM).

As an example the ECC of copper and iron in calcia-aluminosilicate slag are presented in Figure 1. It is noticeable that the application of external voltage to metal-slag boundary may cause the variation of interfacial tension by up to 30% of its initial value.

![Graph showing ECC of copper and iron](image)

**Figure 1:** ECC of copper at 1410°C (left) and iron at 1550°C (right) in slag (mass.%) 40 CaO, 40 SiO2, 20 Al2O3 [3, 4]

The experimental data on the velocities of ECM \((U_E)\) of copper and iron droplets in a similar slag in the horizontal electric field are shown in Figure 2. Even reasonably large droplets, from 3.6 to 5.2 mm in diameter, can move in an electric field faster than in the gravitational field. For smaller droplets the relative effect of external electric field, if compared with the natural precipitation of droplets, is even more pronounced. Therefore, the application of an electric field can be used to control the behaviour of metal-in-slag emulsions.
Practical importance and application of electrocapillary phenomena

Electrocapillary phenomena may play a considerable role in metallurgical processes utilising electric power and in welding, particularly when a source of direct current (DC) is used. In some situations the motion of the metal-slag interface can substantially alter the adsorption of charged species at the interface and thus the electric charge density in the e.d.l. at the phase boundary. This may give rise to the occurrence of electrocapillary effects even without an external power source connected to the system. Like all other capillary phenomena, the electrocapillary effects need to be considered for systems with small enough Weber number, i.e. metal-slag emulsions, porous-capillary bodies, etc.

![Graph](image)

Figure 2. Velocity of ECM ($U_e$) of copper drops (left) [5] and iron drops (right) [4] in slag in a horizontal electric field of strength $E$:
- copper drops - slag (mass.%): 40 CaO, 40 SiO$_2$, 20 Al$_2$O$_3$, temperature 1400°C, radius of drops 2.6 mm, velocity of precipitation in gravitational field ($U_g$) 1 cm/s;
- iron drops - slag (mass.%) 45 CaO, 35 SiO$_2$, 20 Al$_2$O$_3$, temperature 1550°C, radius of drops 1.8 mm, $U_g = 6$ cm/s

Electrocapillary phenomena may affect the motion of metal droplets in slag and their coalescence, mass transfer of components between metal and slag, wetting and corrosion of refractory materials.

Known attempts of use of electrocapillary phenomena for process improvement include:
- recovery of droplets of precious metals from slag;
- separation or sulfide-slag emulsions, e.g., [6];
- deep refining of metal droplets by slag assisted by the application of external electric field;
- control of the emulsification of metal in slag in DC electric arc furnace with bottom argon blowing.

Incorporation of electrocapillary phenomena into kinetic and thermodynamic models of metallurgical processes has a potential to improve the accuracy of the models.
References

Molten Slag Density Measurements with Focus on Slag Structures

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**Keywords:** Density Measurements, Expansivity, Archimedes Principle, Slag structure

Density of molten slags is probably the most important and fundamental thermophysical property playing significant roles in high temperature fluid mechanics and dynamics. In this work, the density of low silica CaO-SiO\(_2\)-Al\(_2\)O\(_3\) slags with a silica content of 5 – 14 % was measured using Archimedes Principle \(^1\). This method has advantage over the other methods for the fact that the oxygen potential can be maintained easily in comparison to the maximum bubble pressure technique and experimental errors can be reduced compared to the sessile drop technique.

The measurement uses a Pt-30%Rh bob which is hung from a balance using a Pt-30% Rh wire. The bob was then immersed in the slag contained in an Armco iron crucible and the change in weight was measured. The crucible material limited the measurements to temperatures 1410 and 1460 °C. The density values obtained from the measurements were later compared with the model developed by Persson et al. \(^2\) and the experimental works of Zielinski and Sikora \(^3\) by the sessile drop technique. Density values of the corresponding binary silicates as well as higher silica ternary slags were then estimated and compared with the experimental works of other researchers.

The density decrease at high temperatures was interpreted based on the silicate structure. As the mole percent of SiO\(_2\) was below the 33 pct required for the orthosilicate composition, discrete SiO\(_4\) tetrahedral units in the silicate melt would exist along with O\(^2-\) ions. The expansivity curve for the ternary system was plotted against the alumina content as shown in Figure 1. The drooping expansivity curve suggested that the predominant expansions in the bonding were due to CaO bonds. The change in melt expansivity may be attributed to the ionic expansions in the order of Al\(^{3+}\) - O\(^2-\) <Ca\(^{2+}\)-O\(^2-\) <Ca\(^{2+}\)-O\(^-\). Structural changes in the ternary slag could also be correlated to a drastic change in the value of enthalpy of mixing.
Figure 1: Expansivity variation with alumina content. Left extreme indicates 51.5% CaO-48.5% SiO₂ binary region and the right extreme indicates the 51.5% CaO-48.5% Al₂O₃ binary.

References

Effect of Bath Chemistry on the Heat Transfer Modelling of Freeze Lining in Copper Containing Slag System

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Key words: Freeze lining, copper containing slag system, deposit, heat transfer

Freeze lining is increasingly used in industrial pyrometallurgical processes to ensure furnace integrity in aggressive environments. To date, the designs of freeze lining for metallurgical reactors have been based solely on heat transfer considerations. However, there is increasing evidence to show that optimum practice should also take into account the effects of bath chemistry. The aim of the present study is to investigate the mechanisms of freeze lining formation and the effects of chemically relevant parameters on the microstructure, stability, thickness and overall heat transfer of freeze lining in steady-state conditions.

In the current research the formation of freeze linings is studied under controlled laboratory conditions in the “Cu₂O”-“Fe₂O₃”-SiO₂-Al₂O₃ system in air. An air-cooled “cold finger” is submerged into the synthetic slag bath contained in a rotating refractory crucible heated in an induction furnace. After a specific time the cold finger with frozen deposit is taken out from the bath and quenched in water. Different submergence times were selected to ensure steady-state-deposit thickness. Optical microscope, scatter electron microscopy and electron probe X-ray micro analysis are used to analyse microstructures and compositions of phases in different layers of deposit and to investigate how they were formed. This information is needed to describe solidification, heat and mass transfer processes that occur during the freeze lining formation.

A general classification of the deposit based on the previous and current studies indicates that freeze-lining deposit consists of several different layers; glassy layer, glass-with-microcrystalline layer, closed crystalline layer, open crystalline layer, primary-phase-crystalline layer and residual bath layer. Based on the observed phases in the deposit-bath interface in a series of experiments, it was found that the bath-deposit interface temperature can be lower than the liquidus temperature of the bulk liquid. The presence solid phases in the deposit in addition to the primary phase crystals are clear indications that the interface between the stagnant layer and the bath liquid is below the liquidus temperature of the system. This supports the concept that there is a transition or boundary layer between the bulk liquid and the deposit interfaces across which there is temperature gradient and possibly a compositional gradient.

Consequently, it is vital to do a systematic study for identification of chemical factors influencing freeze lining thickness and stabilization of the frozen deposit in the steady-state conditions.
Experimental Phase Equilibria Study in Key Low Order Systems for Copper Smelting Slags

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Brisbane, Australia

Key words: key low order systems for copper smelting slags, equilibration, microprobe analysis

It has been an ongoing need in the industry to adequately describe the phase chemistry of complex slag systems using thermodynamic models in order to optimise process performance and improve productivity. The chemical thermodynamic modellings are therefore established for studying complex slag systems, which need to be derived from the experimental study of binary and ternary systems. Those thermodynamic modellings can only be as accurate as the experimental data used in their construction. Therefore, it is essential to obtain the best possible experimental data in the low order slag systems, which is the key to the modelling construction.

In this study, the focus has been on some of the low order systems where (1) discrepancies need to be resolved and (2) new data are required, which have been indicated by evaluating existing experimental data via the initial thermodynamic modellings.

The methodology of this study involves (1) a preliminary phase diagrams are constructed based on phase equilibrium and property data obtained by previous researchers. In the case of sparse data set, theoretical tools together with FactSage were used to help with the design, selection of experimental conditions. (2) the interpretations of experimental phase equilibrium data, which are obtained by using the isothermal equilibration / quenching / microanalysis approach.

Repeated experiments have been conducted at extended equilibration time with compositions from two opposite directions to ensure the achievement of equilibrium. Crucibles are designed to achieve maximum cooling rate. Concentration profiles within the glass (liquid phase) were established to detect incomplete equilibration or any precipitation that may occur during quenching. For an accurate microprobe analysis, standards have been carefully selected and measured comparatively.

One of the systems that have been studied using this approach is “Cu₂O”- CaO- SiO₂ at metallic copper saturation. The objective for studying this system is to investigate the position of the miscibility gap at 1200°C, 1250°C and 1300°C. It was found that the temperature minimum on the miscibility gap boundary line is between 1200°C and 1250°C. The CaO- “Fe₂O₃” system in air is the other system that is currently under study using this approach. The objective was to resolve the discrepancies between FactSage and existing experimental data at temperature below 1350°C.

These studies have provided further insight to these two systems.
Modelling of Thermal Conductivities of Si₃N₄-SiC Refractories and Ti₃SiC₂-SiC Composites

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**Keywords:** Modelling, thermal conductivity, silicon carbide, silicon nitride, titanium silicon carbide, refractory and composite

Silicon nitride bonded silicon carbide (Si₃N₄-SiC) refractories are commonly used as the sidewall of aluminium electrolysis cells. They have to withstand an extremely corrosive molten electrolyte bath for long periods. The sidewall is normally protected with a layer of solidified electrolyte (called frozen ledge), which is sensitive to the thermal conductivity of the sidewall. In the present work, a review of the literature on modelling methods for predicting the effective thermal conductivity of dense composites and porous materials was undertaken. Selected modelling methods were then applied to calculate the effective thermal conductivities of commercial Si₃N₄-SiC refractories and laboratory synthesized Ti₃SiC₂-SiC composites (titanium silicon carbide bonded silicon carbide). The thermal conductivities of two commercial Si₃N₄-SiC refractory samples and eight laboratory synthesized Ti₃SiC₂-SiC composite samples were measured by using laser flash technique and compared with the modelling results.

Through review of the thermal conductivity models reported in the literature, we selected the following modelling methods for evaluation:

- **Method 1:** Maxwell method,¹
- **Method 2:** Method accounting for particle size and interfacial thermal resistance,², ³
- **Method 3:** Method accounting for interfacial thermal resistance, porosity and pore shape,⁴
- **Method 4:** Method based on Effective Continuous Medium (ECM) hypothesis,⁵, ⁶ and
- **Method 5:** Empirical method of Sugawara and Yoshizawa.⁷

Among the selected modelling methods, the Method 3 is capable of modelling three-phase materials comprising of a matrix phase and two dispersed phases (second solid phase and pore), whereas the rest of the methods only account for two-phase materials: a matrix phase and a dispersed phase (either second solid phase or pore). Since the materials investigated in this work are all three-phase materials: a matrix phase (SiC) and two dispersed phases (Si₃N₄ or Ti₃SiC₂ and pore), the present modelling study confirmed that only Method 3 can be applied promisingly in one step. All the other selected modelling methods individually do not give satisfactory predictions in one step and should be used in two or more steps, either recursively or in combinations.

Moreover, all the investigated modelling methods fail to accurately predict the thermal conductivities of materials in which the contact condition in the solid phase is imperfect, i.e., there exist micro gaps between the solid particles. To improve these modelling methods, we
considered solid contact area and radiation and conduction heat transfer inside the micro gaps and examined seven modelling schemes, shown in the following table, for predicting the effective thermal conductivities of the commercial Si$_3$N$_4$-SiC refractories and the laboratory synthesized Ti$_3$SiC$_2$-SiC composites investigated in the present work.

Table 1: Modelling schemes used for predicting the thermal conductivities of Si$_3$N$_4$-SiC refractories and Ti$_3$SiC$_2$-SiC composites

<table>
<thead>
<tr>
<th>Scheme No.</th>
<th>Modelling Step 1</th>
<th>Modelling Step 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Matrix phase</td>
<td>Dispersed phase</td>
</tr>
<tr>
<td>1</td>
<td>SiC</td>
<td>Si$_3$N$_4$ &amp; Pore</td>
</tr>
<tr>
<td>2</td>
<td>SiC</td>
<td>Si$_3$N$_4$</td>
</tr>
<tr>
<td>3</td>
<td>SiC</td>
<td>Pore</td>
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<td>4</td>
<td>Si$_3$N$_4$</td>
<td>Pore</td>
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<td>5</td>
<td>Si$_3$N$_4$</td>
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<td>6</td>
<td>SiC</td>
<td>Pore</td>
</tr>
<tr>
<td>7</td>
<td>SiC</td>
<td>Pore</td>
</tr>
</tbody>
</table>

Note: Replace Si$_3$N$_4$ with Ti$_3$SiC$_2$ for modelling Ti$_3$SiC$_2$-SiC composites.

Among the modelling schemes listed in Table 1, Scheme No. 1 is an application of Method 3 in one step; Schemes No. 2 to No. 4 are recursive applications of a modelling method in two steps; and Schemes No. 5 to No. 7 are combined applications of two modelling methods in two steps.

The present modelling results demonstrate that the above-mentioned modelling schemes are generally universally valid for all the material samples studied in this work, except Schemes No. 2 and No. 5. Scheme No. 2 is only applicable to the materials that are dense or have perfect particle contacts in the solid phase and Scheme No. 5 is only valid for the materials that are very porous or have poor particle contacts in the solid phase. Furthermore, the modelling results also prove that porosity, solid particle size and particle contact conditions in the materials have the most significant influences on the effective thermal conductivities of Si$_3$N$_4$-SiC refractories and Ti$_3$SiC$_2$-SiC composites.

By controlling only two model parameters, namely, the particle boundary contact factor, $f_c$, and the empirical parameter, $n$, all the selected modelling methods can be effectively applied in certain ways (i.e., individually, recursively or in combinations) for predicting the effective thermal conductivities of the commercial Si$_3$N$_4$-SiC refractories and the laboratory synthesized Ti$_3$SiC$_2$-SiC composites investigated in this work. Through considering contact area and radiation and conduction heat transfer at particle boundaries with imperfect contact conditions, the accuracy of the selected modelling methods can be significantly improved, as shown in Figure 1.
Figure 1: Comparison between the thermal conductivities predicted, with the same modelling scheme (No. 1), by using the previous modelling method for perfect solid contact conditions and the improved modelling method for imperfect solid contact conditions.
(Note: 312 means Ti$_3$SiC$_2$.)

References

Gasification of Coke with CO₂

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Key words: gasification, coke, carbon dioxide, kinetics, porosity

Gasification of coke with carbon dioxide is a major reaction in ironmaking and carbothermal reduction of alumina, titania and other metal oxides. This paper examines the effects of temperature, CO₂ partial pressure, gas flow rate and particle size on the rate of coke gasification by CO₂.

Coke gasification was studied in a fixed bed reactor in the CO₂-Ar gas mixture. Coke pieces were crushed using a jaw crusher and then sieved into different particle size ranges. Unless specifically indicated, the size range used in this investigation was 500 – 800 μm (with an average size of 650 μm), the gas flow rate was 1 NL/min, and the CO₂ partial pressure was 6 kPa. 1 g of coke was loaded in each experiment except those examining the effect of gas flow rate in which the weight changed from 0.5 to 2.0 g corresponding to the increase of gas flow rate from 0.5 to 2 NL/min. The experimental conditions are listed in Table 1.

Table 1: Experimental conditions of gasification reaction

<table>
<thead>
<tr>
<th>Parameter examined</th>
<th>Temperature (°C)</th>
<th>Total pressure (kPa)</th>
<th>CO₂ partial pressure (kPa)</th>
<th>Gas flow rate (NL/min)</th>
<th>Particle size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>900–1500</td>
<td>100</td>
<td>6</td>
<td>1</td>
<td>650</td>
</tr>
<tr>
<td>CO₂ partial pressure</td>
<td>1100</td>
<td>100</td>
<td>2–10</td>
<td>1</td>
<td>650</td>
</tr>
<tr>
<td></td>
<td>1400</td>
<td>100</td>
<td>2–10</td>
<td>1</td>
<td>650</td>
</tr>
<tr>
<td>Gas low rate</td>
<td>1100</td>
<td>100</td>
<td>6</td>
<td>0.5–2</td>
<td>650</td>
</tr>
<tr>
<td></td>
<td>1400</td>
<td>100</td>
<td>6</td>
<td>0.5–2</td>
<td>650</td>
</tr>
<tr>
<td>Particle size</td>
<td>1100</td>
<td>100</td>
<td>6</td>
<td>1</td>
<td>400–1100</td>
</tr>
<tr>
<td></td>
<td>1400</td>
<td>100</td>
<td>6</td>
<td>1</td>
<td>400–1100</td>
</tr>
</tbody>
</table>

1. Effect of Temperature

The relationship between the apparent reaction rate and the extent of carbon conversion is shown in Figure 1. The gasification rate increased with increasing temperature from 900°C to 1500°C. At 900-1200°C, the rate of carbon gasification increased at the initial reaction stage, reached maximum at 2% carbon conversion and decreased with further gasification. The rate of gasification at 1100°C was higher than at 1200°C when the extent of reaction was below 20%, what was also observed in gasification of graphite with addition of iron[1], and can be explained by catalytic effect of iron in coke ash. In the temperature interval 1300-1500°C, the rate of carbon gasification increased with increasing extent of reaction. A complex effect of
temperature on coke gasification can be explained by the development of pore structure which is currently under investigation.

Figure 1: Gasification of coke at different temperatures, (a) 900-1200°C, (b) 1300-1500°C.

2. Effect of CO₂ Partial Pressure, Gas Flow Rate and Particle size

The effects of the CO₂ partial pressure (2-10 kPa), flow rate of the CO₂-Ar gas mixture (0.5-2.0 L/min) and particle size (400µm to 1100µm) on the rate of carbon gasification were examined at 1100°C and 1400°C. In the study of the effect of the gas flow rate, the sample mass increased proportionally to the gas flow rate as described above.

The gasification rate increased with increasing CO₂ partial pressure at both temperatures. However, the change in the reaction with the extent of gasification at 1100°C was different from that at 1400°C. Increasing gas flow rate increased the gasification rate at 1100°C and had no effect on the gasification at 1400°C.

The reaction rate increased with decreasing particle size at 1100°C. While at 1400°C, the reaction rate was not affected by the particle size.

It can be concluded that the reaction mechanism and rate control in coke gasification are different at 1100°C and 1400°C. Their understanding requires further examination of gasification reactions which is currently in progress.

References

Phase Equilibria and Preliminary Viscosity Studies of “Cu₂O”-SiO₂ –Al₂O₃ Systems in Equilibrium with Metallic Copper

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Keywords: phase equilibria, viscosity measurements, EPMA, Cu₂O-SiO₂-Al₂O₃

Present study is a part of an overall program on development of the accurate viscosity model of the complex multi-component slag (molten oxide) for Cu production. Copper converting slag, in which contain high concentrations of Cu₂O and SiO₂ with some other components such as Al₂O₃ and iron oxides, need to be carefully investigated. Very limited phase equilibrium information and no viscosity data were found in literature in “Cu₂O”-SiO₂-Al₂O₃ system at Cu saturation condition.

In the present study, the phase diagram of “Cu₂O”-Al₂O₃-SiO₂ system at metallic copper saturation condition has been constructed parallel to the development of viscosity measurement technique. High temperature equilibration and rapid quenching techniques were used to study the phase equilibria. The primary phases and liquidus temperature between 1423 K (1150 °C) and 1573 K (1300 °C) have been determined. The experiments were carried out in Ar gas atmosphere using different substrates (Al₂O₃, SiO₂, and etc.) as containment material. The compositions of all phases present in the slag were measured accurately using electron probe X-ray micro-analysis (EPMA). Under experimental conditions, there are both Cu⁺ and Cu²⁺ presented in the samples. However, only the metal cation concentrations can be measured using EPMA, so the phase compositions are usually recalculated to “Cu₂O” on the assumption that all copper is presented as Cu⁺. The following primary phase fields were identified in the system: SiO₂ (tridymite), Cu₂O (cuprite), Cu₂O-Al₂O₃ (delafosseite), Al₂O₃ (corundum) and 3Al₂O₃,2SiO₂ (mullite). The ratio of Al₂O₃/SiO₂ was found almost fixed along the liquidus lines at high “Cu₂O” concentration in “Cu₂O”-SiO₂-Al₂O₃ system.

The technique of viscosity measurement in Cu₂O containing system at Cu saturation condition was developed. The difficulty was that the aggressive slag reacts and dissolves any ceramics, and molten metallic copper reacts and dissolves any noble metal (e.g. Pt, Rh), so that the combination of the slag and molten copper makes it practically difficult to select material for crucible and spindle for experimental viscosity measurements. Current development was based on one of the essential features found from the equilibrium studies that there is a limited solubility of Al₂O₃ in the “Cu₂O”–Al₂O₃ melt and slow solubility of Al₂O₃ in the “Cu₂O”-SiO₂-Al₂O₃ melt at metallic copper saturation. Therefore, the viscosity measurements were carried out in the “Cu₂O”-Al₂O₃ and “Cu₂O”-SiO₂-Al₂O₃ systems in equilibrium with metallic copper in the vicinity of the “Cu₂O” and “Cu₂O”-SiO₂ systems respectively using Al₂O₃ crucible and spindle.

The custom designed rotating bob apparatus enables control of the gas atmosphere and rapid quenching of the samples on completion of the experiment ¹). The microstructures and phase compositions in the quenched slag samples are determined by Electron Probe X-ray Microanalysis (EPMA). The analysis of the composition across the quenched samples in the
“Cu₂O”-SiO₂-Al₂O₃ system performed with EPMA showed that the liquid slag composition is uniform after a short distance away from the crucible/slag interface.

It is believed that the present experiments that being reported are the first experimental measurements of viscosities in this high “Cu₂O” slag system in equilibrium with metallic Cu. New viscosity data in the “Cu₂O”–rich corner of the “Cu₂O”-SiO₂-Al₂O₃ system at metallic copper saturation will be used to optimise parameters of the revised quasi-chemical viscosity model ²⁻⁴).

Reference

Micro-properties of Carbonaceous Materials

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Key words: carbonaceous materials; annealing; microstructure; XRD; Raman spectroscopy

Carbonaceous materials are highly porous, therefore their properties depend on both pore structure and properties of wall which contains inert maceral-derived component (IMDC) and reactive maceral-derived component (RMDC). Upon heating in metallurgical processes, significant changes can be expected in wall properties of carbonaceous materials as a result of graphitisation.

This paper examines the effect of annealing at 700–1500 °C on the microstructures of carbonaceous materials using XRD and Raman spectroscopy. The carbonaceous materials examined in this study included metallurgical cokes, chars and coals. The coal samples were processed at 700°C in argon atmosphere to remove volatile matter to obtain laboratory char samples. Then coke and char samples were further annealed in a graphite furnace in argon atmosphere for 2 hours at 700, 900, 1100, 1300 and 1500°C.

The microtexture of original coke and char (IMDC and RMDC), and that of carbonaceous materials after heat treatment at 1500 °C for 2 h are presented in Tables 1 and 2, respectively.

| Table 1: Microtexture of original coke and char samples, % |
|-----------------|-------|-------|-------|
| Sample          | RMDC  | IMDC  | Other |
| Coke 1          | 61.6  | 38.4  | 0.0   |
| Coke 2          | 62.5  | 37.5  | 0.0   |
| Coke 3          | 75.4  | 24.6  | 0.0   |
| Char 1          | 17.0  | 58.7  | 24.3  |
| Char 2          | 0.0   | 53.3  | 46.7  |
| Char 3          | 0.6   | 99.4  | 0.0   |

Coke samples contained both RMDC and IMDC, with RMDC being a major component in the microtexture of coke before and after heat treatment. The microtexture of chars and coals after heat treatment was predominantly IMDC. The appearance of “Other” in Table 1 differed
from the standard optical textures of cokes, which are identified as RMDC or IMDC, and was similar to low-rank coal. This char texture was resulted from incomplete pyrolysis and condensation during char production. Char 1 and Char 2 contained 24.3% and 46.7% of this type of microtexture, which changed to IMDC after further heat treatment at 1500 °C (Table 2).

Table 2: Microtexture of carbonaceous materials after heat treatment at 1500 °C for 2h, %

<table>
<thead>
<tr>
<th>Sample</th>
<th>RMDC</th>
<th>IMDC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coke 1</td>
<td>59.6</td>
<td>40.4</td>
</tr>
<tr>
<td>Coke 2</td>
<td>70.1</td>
<td>29.9</td>
</tr>
<tr>
<td>Coke 3</td>
<td>66.3</td>
<td>33.7</td>
</tr>
<tr>
<td>Char 1</td>
<td>16.0</td>
<td>84.0</td>
</tr>
<tr>
<td>Char 2</td>
<td>2.4</td>
<td>97.6</td>
</tr>
<tr>
<td>Char 3</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Coal 1</td>
<td>0.4</td>
<td>99.6</td>
</tr>
<tr>
<td>Coal 2</td>
<td>3.0</td>
<td>97.0</td>
</tr>
<tr>
<td>Coal 3</td>
<td>1.1</td>
<td>98.9</td>
</tr>
</tbody>
</table>

The crystallite size $L_c$ and interlayer spacing between aromatic planes of carbon crystallites $d_{002}$ were measured by XRD and calculated using the Scherrer equation and Bragg’s Law. G fraction (proportion of graphite) and D fraction (proportion of disordered carbon) were measured using Raman spectrum.

The crystallite size and G fraction increased while the D fraction decreased with increasing annealing temperature. The degree of graphitisation of all materials tested increased as annealing temperature rose, particularly in the range of 1100–1500 °C. Raman spectroscopy of inert and reactive maceral-derived components showed that both the degree of graphitisation and the effect of temperature on graphitisation were higher for the reactive maceral-derived component than for the inert maceral-derived component.

The G fraction is correlated with $L_c$ for all carbonaceous materials annealed in the temperature range 1100–1500 °C (Figure 1). Graphitisation by annealing simultaneously increased both the G fraction in the Raman spectra and the crystallite size of graphite grains. The trend line in Figure 1 showed that with a 10% increase in the G fraction, $L_c$ increased from 12 to 50 Å. An increase in $L_c$ can be caused by stacking of two or more graphitic units to form a larger graphite crystallite. The increase in the G fraction is not directly proportional to the change in $L_c$.

The major findings of this investigation are summarised below.

1. RMDC was the major maceral-derived component of cokes before and after heat treatment, whereas the microtexture of chars and heat-treated coals was predominantly IMDC.
2. Heating of carbonaceous materials increased the degree of graphitisation. This conclusion follows from a reduction of the interlayer spacing ($d_{002}$) between aromatic planes, an increase of the stack height ($L_c$) of graphite crystallites, and G fraction in the Raman spectra.
3. Cokes had a lower interlayer spacing and larger stack height and G fraction than chars, which is consistent with the higher degree of their graphitisation.
4. A significant growth in graphite crystallite size, demonstrated by $L_c$, took place at annealing temperatures above 1100 °C.
5. The graphitisation degree of RMDC was higher than that of IMDC, and annealing had a stronger effect on the graphitisation of RMDC than on IMDC.

![Graph showing the relationship between $L_c$ and G fraction for carbonaceous materials subjected to heat treatment at 1100–1500 °C]

**Figure 1:** Correlations between $L_c$ and G fraction for carbonaceous materials subjected to heat treatment at 1100–1500 °C

**References**

ADDITIONAL EXTENDED ABSTRACT

Two Problems for Liquid Metal Viscometry:
non-Newtonian Fluid Flow and Combined Viscosity/Density Measurement

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Keywords: oscillating-cup viscometer, non-Newtonian fluids, density

Oscillating-cup viscometer (OCV) is the main method to measure properties of liquid metals and alloys in both condensed matter physics and metallurgical industry. The technique is widely used for their study from the middle of last century (e.g., [1]) to the present time (e.g., [2]). This is determined by a number of reasons related, e.g., to high temperature, chemical reactivity and low melt viscosity. Construction simplicity, absence of immersion probe, ease in using an inert atmosphere and inactive materials, small volume samples and i.e. isothermality, etc. allow to create adequate experiment conditions and eliminate some factors leading to incorrect interpretation of data.

Recently, the problem of non-Newtonian behaviour of liquid metals and alloys has been actively discussed (e.g., [3]) including the experiments with rotational viscometer. It is, therefore, very timely to draw attention to the problem at data processing in oscillating-cup technique where traditional approach is developed only for Newtonian fluids. Analysis of observability of nonlinear rheological effects in OCV and constructing the corresponding theory are carried out, e.g., in [4]. For practice, an analytical solution is of interest for which we developed the algorithm using an interpretation and exact formulas in terms of linear fluids with averaging on period and inside viscometer surface. Some practical applications based on these viscometric equations are in [5]. Here we demonstrate the basic features separating the types of behaviour of Newtonian and other fluids in viscometer and we focus on power law fluids with flow consistency k and behaviour m indexes. Note that neglect by non-Newtonian fluid type can be one of reasons of the known contradictions in viscometric data obtained by OCV.

For Newtonian fluids, we introduce \( A = 0.5 MR^2 / K \), \( \xi_0 = R / \sqrt{\nu \tau_0 / (2 \pi)} \), \( \chi = H / R \), where \( H \), \( R \) and \( M \) are the sample height, radius and mass; \( K \) is the moment of inertia of empty cup system; \( \tau_0 \) and \( \delta_0 \) are the period \( \tau \) and decrement \( \delta \) of oscillations at \( M = 0 \); \( \nu \) is the kinematic viscosity. With increasing \( \xi_0 \), \( \tau \) decreases mainly at \( \xi_0 \in (2, 12) \) (Fig. 1). Dependence \( \delta(\xi_0) \) has maximum at some \( \xi_m \) and \( \delta \rightarrow \delta_0 \) for \( \xi_0 \rightarrow 0 \) or \( \xi_0 \rightarrow \infty \). Value \( \xi_m \sim 4.5 \) for long cylinder, i.e. for \( \chi \rightarrow \infty \), and \( \xi_m \) shifts to larger \( \xi_0 \) for smaller \( \chi \). When relation of the moments of inertia \( A \) increases, these curves become steeper.

![Figure 1: \( \bar{\lambda} = \xi / \tau^2 \) (1) and \( \delta \) (2) \( A = 0.1 \), \( \chi \rightarrow \infty \)](image)

Oscillations of viscometer filled with linear fluids, including viscoelastic ones, are linear out the transient, i.e. decrement and period are constant in time. For viscometer filled with
nonlinear fluids, they change in oscillation process and it has stable dynamics not associated with external random factors. For nonlinear viscous fluids, the effective value 
\[ \tilde{\xi}_{\text{eff}} = \frac{\tilde{\xi}_0}{\sqrt{bD^{m-1}}}, \]
where \( b = k(v\rho)^{-1}(2\pi/\tau_0)^{m-1} \) and \( D \) is the dimensionless shear rate, \( D < 1 \) for oscillating-cup experiments when the initial angular displacement of cylinder from equilibrium \( \alpha_0 \sim 6^\circ \). In the damping, amplitude of \( D \) decreases, effective viscosity \( \nu_{\text{eff}} \) and \( \tilde{\xi}_{\text{eff}} \) change and the corresponding changes of \( \tau \) and \( \delta \) depending on number of oscillation \( N \) from the beginning are taken place.

For pseudoplastic fluids, \( \nu_{\text{eff}} \) increases, i.e. \( \tau \) increases and \( \delta \) passes through maximum if \( \tilde{\xi}_m < \tilde{\xi}_{\text{eff}} \) at \( N \sim 1 \), for dilatant fluids – vice versa (Fig. 2). E.g., \( \tilde{\xi}_{\text{eff}} \sim 4.5 \) responds to the extreme in Fig. 2b. After solidus, the averaged on \( N \) values of \( \delta \) and \( \tau \) change similarly the curves in Fig. 1 with \( \tilde{\xi}_0 \). Points in these curves are determined by viscosity and shear rate responding Newtonian fluid for given experimental conditions. For nonlinear flow, such values are corrected from velocity field for linear fluids, e.g., by the method of approximations. Oscillating-cup technique is of high precision of measurements, the accuracy of direct measurements of oscillation parameters, e.g., of \( \tau \) is \( \sim 10^{-4} \) and the changes as in Fig. 2 are observable. Forced mode extends working range of viscous and, especially, elastic properties. It allows to use OCV for various classes of nonlinear fluids, and not only high-temperature ones, and also to use the algorithm for any oscillatory viscometry including external flow. Approach to analysis of alloys as non-Newtonian fluids can be also useful to relate kinetics of solidification with their rheological properties or, e.g., to determine liquidus from change of flow behaviour.

The mathematical model of viscometric experiment includes, besides rheological constants, also density \( \rho \) that allow to suggest their simultaneous measurement, i.e., from the same experiment [6]. It gives possibility to study fluids with weakly investigated equations of state, to eliminate errors caused by difference in temperature and pressure for independent measurements of \( \nu \) and \( \rho \) and to check the consistency of data. But for high-temperature cases, i.e., for lower accuracy, and cylinder geometry, the task is complicated by the facts that we consider on the example of Newtonian fluid and the corresponding viscometric equation (see, e.g. (9)–(11) in [4]). Here density is only included in end-wall term of the friction function \( L \) and is absent in term for lateral surface of cylinder, i.e., it is impossibly to find \( \rho \) for \( \chi \to \infty \). Also main difficulties are that errors in \( \nu \) and \( \rho \) are correlated and, e.g., there is
high sensitivity to errors in $\tau$ through imaginary part of this viscometric function. This can lead to errors in density up to thousand percents and it requires to make an optimal experiment design in detail.

Behaviour of oscillation parameters in Fig. 1 gives intervals of working sensitivity of fluid properties to characteristics $x$ observed in experiment ($x$ is $K$, $R$, $\tau$, etc.): e.g., for Newtonian fluid at $\xi_0 \sim \xi_n$, error in viscosity is too high. Sensitivity of density to these parameters $\psi_{\rho, x} - \psi_{\nu, x}$, where $\psi_{\rho, v}$ increases with $H$ and $\psi_{\nu, v}$ conversely decreases (e.g., in view of $A$), ceteris paribus. Effective estimation algorithm takes into account an analysis and choice of combinations of different experimental points, setting the weight coefficient for different parts of $L$, etc. The developed methods for parameter identification include analysing the model identifiability in terms of Jacobi matrix, creating the quality function, finding the components of covariance matrices of unknown parameters from measurable values, testing the model adequacy and choosing the optimal experiment conditions on the basis of sensitivity theory.

Thus, OCV can be considered as an instrument to measure both kinematic and dynamic viscosities or other rheological constants. The work was partially supported by the Russian Foundation for Basic Research (N 10-01-96042-ural, 10-08-00536).

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