CHARACTERIZATION METHODOLOGY FOR COPPER-DROPLET LOSSES IN SLAGS

Evelien De Wilde and Kim Verbeken
Ghent University - Department of materials science and engineering
Technologiepark Zwijnaarde 903
9000 Gent, Belgium
evelien.dewilde@ugent.be

Mieke Campforts and Stephanie Vervynckt
Umicore R&D
Kasteelstraat 7
2250 Olen, Belgium

Kim Vanmeensel and Nele Moelans
Leuven University – Department of metallurgy and materials engineering
Kasteelpark Arenberg 44, bus 2450
3001 Hevelee, Belgium

Greetje Godier
Flamac, a division of SIM
Technologiepark 903
9052 Zwijnaarde, Belgium

ABSTRACT

A major cause of metal losses in slags is the mechanical entrainment of metal droplets. One important factor is the attachment to solid spinel particles in the slag phase. Consequently, these particles hinder the settling of the metal droplets. In order to improve phase separation it is important to identify the fundamental mechanisms governing this attachment. Two complementary methodologies have been developed to study the tendency of metal droplets to attach to solid spinel particles. In one methodology, the interaction between Cu-alloys and spinel is studied by high temperature contact angle measurements. In the other, the entrainment is studied using a synthetic slag containing spinel solids.
INTRODUCTION

Slags play an essential role in pyrometallurgical processes acting as collectors for specific groups of metals and for the elimination of unwanted impurities. Decantation is often the last step in pyrometallurgical processes, allowing the phase separation between slag and matte/metal. However, industrial Cu smelters still suffer from metal rich droplet losses in slags due to insufficient phase separation. In order to realize an improvement of copper smelting and recycling processes and to minimize these metal losses, it is essential to gain fundamental knowledge concerning the form and origin of these losses.

Based on extensive research, it is currently well accepted that metal losses in slags are mainly caused by chemical dissolution in oxidized form and mechanical entrainment [1-3]. Chemical dissolution of copper is intrinsic to pyrometallurgical processes as its occurrence is determined by the thermodynamic equilibrium of the system such as the chemical activity of the metal [1], slag/matte phase [1, 4-6], the partial oxygen pressure [1, 4-6], the temperature of the system [1,6] and the reaction time. Mechanically entrained metal droplets can arise from a variety of sources like charging or tapping [7-8], metal precipitation from slag due to temperature fluctuations [9], gas producing reactions dispersing metal into the slag [9-11] or attachment to solid particles in the slag [9]. The first three main sources have been studied extensively in literature. Concerning the latter, available literature and fundamental knowledge is scarce; nevertheless this phenomenon is industrially relevant as the attachment of Cu-alloy droplets to spinel particles is found to cause metal losses in the slag. The specific and complex nature of the mechanisms responsible for this phenomenon, warrant a fundamental and systematic investigation.

The present study aims to develop a methodology to study the interaction between Cu droplets and spinel particles in industrial systems. To our knowledge, no systematic evaluation on the specific interactions responsible for this attachment phenomenon has been performed in literature so far. In order to gather the desired know-how on this interaction, two complementary methodologies have been developed, as represented in figure 1 [12]. On one hand, the interaction of Cu with spinel particles present in the synthetic slag system PbO-Cu₂O-CaO-SiO₂-Al₂O₃-ZnO-FeO is examined. The experimental methodology for the melting experiments is based on the decantation of one bigger Cu droplet through the slag system with a well-chosen synthetic composition in the single-phase region of the slag system. In order to increase the possible interaction, the slag is saturated with alumina, leading to a spinel layer at the interface between the slag system and the alumina crucible. In a first series of experiments, the methodology to study the metal droplet-solid-slag interaction has been developed, which has been described extensively by De Wilde [12].
Additional a methodology for high temperature contact angle measurements has been developed in order to study the interaction between Cu-droplets with spinel substrates in the absence of a slag system, using contact angle measurements at high temperature. First steps in the development of this methodology have been described by De Wilde [12]. This paper describes the further optimization of this methodology and discusses the first experimental results of the interaction between MgAl$_2$O$_4$ substrates and pure copper.

**EXPERIMENTAL SECTION**

A conventional method to investigate interfacial interaction between a substrate and a liquid is observing the wetting behaviour of the liquid on the substrate, quantified by the contact angle. Analogously contact angle measurements between spinel substrates and Cu-alloys under varying atmosphere could yield the important influencing factors on the interfacial interactions between spinel and Cu-alloys. However, contact angle measurements are not evident for the current system. High temperatures have to be obtained in order to melt Cu and Cu-alloys ($T_{M\,Cu} = 1083^\circ$C). Moreover, Cu-smelters work at temperatures of 1100°C-1300°C. Consequently standard contact angle measurement equipment cannot be used.
In order to be able to perform high temperature contact angle measurements with comparable results, measurements have to be executed using a repeatable and reproducible methodology. A suitable setup has to be developed and spinel substrates have to be produced. Furthermore the presence of surface active species such as oxygen and sulphur has to be fully controlled in order to avoid unknown and unwanted effects.

**Optimization Experimental procedure Contact angle**

**Production spinel substrates**

Contact angle measurements demand good substrates. More specific substrates for contact angle measurements should be dense, with minimal porosity, chemical homogeneous, free of thermal stresses and produced in a reproducible way. For the production of spinel substrates, a powder metallurgical process was chosen. Two commercially available spinel powders were selected as the starting material: MgAl$_2$O$_4$ and ZnFe$_2$O$_4$.

For the production of MgAl$_2$O$_4$ spinel substrates, the spark plasma sintering equipment is used as described by Vanmeensel and co-workers [13], based on previous experiments from Wang, Morita and Frage [14-16]. The MgAl$_2$O$_4$ powder (<50 nm particle size, Sigma Aldrich) was sintered under a load of 60 MPa at a temperature of 1300°C. The MgAl$_2$O$_4$ plates were subsequently annealed at 1000°C for 3 hours. The sintered and annealed MgAl$_2$O$_4$ samples were polished using a 1-3-9 µm diamond paste, while a finishing step using colloidal silica was applied. More details concerning the sintering process are described by De Wilde [12].

ZnFe$_2$O$_4$ substrates were produced using a ‘free sintering’ approach. ZnFe$_2$O$_4$ powder (<100 nm particle size, Sigma Aldrich) was first compressed in pellets (1.2 cm diameter) using a cold press, using a pressure of 5N. The pellets were subsequently isostatically pressed with 2500 bar (= 33 kN). These compressed plates were then sintered in air in a tubular furnace at 1200°C for 3 hours. Finally an annealing step was performed during 2h at 1000°C. The sintered and annealed ZnFe$_2$O$_4$ samples were polished using a 1-3-9 µm diamond paste, while a finishing step using colloidal silica was applied. An XRD diffractometer (Siemens diffractometer D 5000) was used for identifying the spinel phase in the ‘free sintered’ substrate. The XRD pattern is shown in figure 3. All the diffraction peaks can be indexed to the cubic spinel structure of ZnFe$_2$O$_4$ (International centre for diffraction data, No 01-070-6394). This indicates that the free sintering does not have any influence on the chemical composition of the ZnFe$_2$O$_4$. Representative optical micrographs of the
polished substrate can be seen in figure 2. An average Vickers harness of HV-3 of 524.4 ± 11.8 was obtained, the density of the ZnFe$_2$O$_4$ substrate is 4.91 g/cm$^3$.

![Image of optical microscopy pictures substrate](image)

**Figure 2**– optical microscopy pictures substrate

![Image of XRD pattern](image)

**Figure 3**– XRD pattern of ZnFe$_2$O$_4$ substrate obtained by free sintering and reference diffraction peaks (red) of ZnFe$_2$O$_4$ (International centre for diffraction data, No 01-070-6394)

Production of copper alloys

Copper alloys for the contact angle measurements have been produced using an inductive microgranulation furnace (Indutherm). Three industrial relevant alloying elements have been selected: Lead, Silver and Nickel. Components have been weighed and melted in
an adapted graphite crucible in the microgranulation furnace. The mixing of the alloying elements is driven by the magnetic field.

Table 1 – Oxygen level alloys before and after treatment with CO

<table>
<thead>
<tr>
<th>Cu-alloy</th>
<th>Oxygen level before treatment with CO (ppm)</th>
<th>Oxygen level after treatment with CO (ppm)</th>
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<tbody>
<tr>
<td><strong>Cu-Ni alloys</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 W% Ni</td>
<td>70</td>
<td>2</td>
</tr>
<tr>
<td>10 W% Ni</td>
<td>600</td>
<td>14</td>
</tr>
<tr>
<td>15 W% Ni</td>
<td>680</td>
<td>13</td>
</tr>
<tr>
<td><strong>Cu-Ag alloys</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 W% Ag</td>
<td>850</td>
<td>70</td>
</tr>
<tr>
<td>12.5 W% Ag</td>
<td>2500</td>
<td>19</td>
</tr>
<tr>
<td><strong>Cu-Pb alloys</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 W% Pb</td>
<td>1600</td>
<td>5</td>
</tr>
<tr>
<td>12.5 W% Pb</td>
<td>700</td>
<td>7</td>
</tr>
<tr>
<td>30 W% Pb</td>
<td>730</td>
<td>22</td>
</tr>
</tbody>
</table>

The oxygen content of the granules should be controlled due to its surface active properties. Therefore the granules are subsequently re-melted two times under a reductive CO atmosphere in an induction furnace in order to diminish the oxygen content in the granules. LECO-oxygen analyses have confirmed the diminishing of the oxygen content in the alloy, as shown in table 1.

For the contact angle measurements, an adapted confocal scanning laser microscopy (CSLM) with an infrared heating image furnace (1LM21SVF17SP) set-up is used. This set-up allows rapid and slow heating and cooling, and high precision temperature holding. At sample height, a window is placed at the side of the heating chamber. Furthermore, a camera (Ganz ZC-F10C3) is placed on the same height. These adaptations, which are shown in figure 4, allow monitoring the interaction between the spinel substrate and the copper(-alloy) in time. An image of a Cu-droplet with at MgAl₂O₄ substrate at 1250°C is shown in figure 5.
Figure 4– Adaptations on the CSLM set-up for contact angle measurements

Due to direct heating of the sample by focussing the radiation from a 1.5 KW Halogen lamp by the gold coated elliptical heating chamber, fast heating and cooling rates can be obtained. This enables to freeze the contact angle between the spinel substrate and the copper at high temperature, which could be observed by comparison of the image of the substrate at high temperature and after solidification. Therefore the contact angle of the solidified droplet is determined (FTA 2000, First Ten Ångstroms, FTA32 software), as illustrated in figure 5.

Figure 5– Adaptations on the CSLM set-up for contact angle measurements

Interaction MgAl2O4 – Copper : Initial experiments
Initial experiments using this methodology have been performed using pure copper and MgAl₂O₄ substrates. The experiments were persecuted under an argon atmosphere, which has been treated with silica to remove water and magnesium (at 500°C) to reduce the oxygen content. Before the experiment, the copper piece was etched using a 1:1 HCl:H₂O solution, to remove a possible oxidized copper outer layer. Subsequently the substrate and the copper were placed in the adapted CSLM set-up, and the heating chamber was flushed three times with Ar. Subsequently the temperature was gradually increased until 300°C with a heating rate of 50°C. After 1 min at 300°C the temperature was further increased until 1050°C with a heating rate of 200°C. After 5 min at 1050°C the temperature was increased until 1250°C which was maintained for 10, 60 and 120 minutes. Finally the sample is quenched with a cooling rate of 500°C/min. A view of the copper droplet on the spinel substrate at 1250°C for each experiment is shown in figure 6.

Figure 6– Interaction spinel substrates and copper at high temperature

<table>
<thead>
<tr>
<th>Time at 120°C</th>
<th>Contact angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 min</td>
<td>111.72° ± 6.99°</td>
</tr>
<tr>
<td>60 min</td>
<td>111.02° ± 4.02°</td>
</tr>
<tr>
<td>120 min</td>
<td>118.45° ± 8.12°</td>
</tr>
</tbody>
</table>

The contact angles of the solidified samples are listed in table 2. A non-wetting behaviour is observed between the spinel substrate and the copper. Furthermore, no marked changes in the contact angle of the solidified samples can be noticed.

Subsequently the samples were embedded, grinded and polished in order to study the interaction area between the substrate and the droplet. Scanning electron images at interface between the MgAl₂O₄ substrate and the copper from the three samples are shown in figure 7. Electron probe microwave dispersive measurements confirmed the presence of small cavities between the spinel substrate and the solidified copper droplets, which can be observed in figure 7.
CONCLUSIONS

The methodology of the contact angle measurements at high temperature has been further optimized, in order to study the interaction between Cu-droplets and spinel substrates in the absence of a slag system. The combination of this methodology with the melting experiments could be very useful to reveal fundamental information considering the interaction between Cu-alloys and spinel particles in industrial Cu-smelters.

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