Towards a methodology to study the interaction between Cu droplets and spinel particles in slags.

M. Sc. Evelien De Wilde[a], Inge Bellemans[a], Prof. Dr. Ir. Stephanie Vervynckt[b], Dr. Ir. Mieke Campforts [b], Dr. Ir. Kim Vanmeensel[c], Prof. Dr. Ir Nele Moelans[c], Prof Dr. Ir Kim Verbeken [a]

a : Ghent University (UGent)

Department of Materials and Science Engineering

Technologiepark, 903

B-9052 Zwijnaarde (Ghent)

Belgium

b : Umicore Research

Kasteelstraat 7

B-2250 Olen

Belgium

c : Leuven University (KU Leuven),

Department of Metallurgy and Materials Engineering

Kasteelpark Arenberg 44, bus 2450

B-3001 Heverlee (Leuven)

Belgium

Abstract

Industrial Cu-smelters still suffer from metal rich droplet losses in slags due to insufficient phase separation. One important factor in the mechanical entrainment of metal rich droplets in slags is their attachment to solid spinel particles, which are also present 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 mechanism governing this attachment.

Industrial slags are, however, of an extremely complex nature and, therefore, the entrainment of Cu-alloy droplets is studied in this work in a simplified, synthetic PbO based slag (PbO-CaO-SiO_2-Cu_2O-FeO-ZnO) containing solid spinel particles. This work presents results on the development and optimization of a methodology to characterize the synthetic system and to discover trends in the interaction at the interface between the spinel and Cu-metal phase.

I. Introduction

Slags play an essential role in pyrometallurgical processes acting as collectors for specific groups of metals and for the elimination of unwanted impurities. Although desirable, a perfect

phase separation is impossible and valuable metal losses are inevitable during these processes and, consequently, an important issue in metal extraction industries. In order to minimize these losses and further increase efficiencies of industrial processes, it is essential to determine the form and origin of the metal losses.

Extensive research has been performed on Cu losses in the slag phase during Cu processing and refining processes. Currently, it is accepted that copper losses in slags are caused by chemical dissolution of copper and mechanical entrainment of Cu containing droplets.[1-3]

Chemical dissolution of metals is inherent to pyrometallurgical processes and its occurrence is governed by the thermodynamic equilibrium of the system: The chemical activity of the metal[1], the chemical composition of the slag/matte phase[1; 4-6], the partial oxygen pressure[1; 4; 6] and the temperature of the system[1; 6].

Mechanically entrained metal droplets can originate from a variety of sources. Three sources have been discussed in detail in literature based on scientific research using both simplified and industrial slag systems:

- entrainment due to charging of the furnace or tapping of the slag[7; 8],
- precipitation of metal from the slag due to temperature fluctuations[9] or chemical reactions,
- gas producing reactions (e.g. SO_2-formation), dispersing the metal into the slag phase, as the gas crosses the metal-slag interface [9-11].

There is however a fourth possible source on which only scarce literature data are available, namely the mechanical entrained Cu rich droplets due to their attachment to solid particles present in the slag. An industrial example is the attachment of Cu rich droplets, to spinel particles present 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 the study the interaction between Cu droplets and spinel particles in a slag. 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, a dedicated experimental methodology needs to be developed and optimized. First, the interaction of Cu with spinel particles present in the synthetic slag system PbO-Cu_2O-CaO-SiO_2-Al_2O_3-ZnO-FeO is examined. Subsequently, the production of spinel substrates for high temperature contact angle measurements of Cu droplets in contact with the spinel phase is discussed.

II. Experimental procedure

A synthetic PbO based slag system has been chosen in this work: PbO-Cu_2O-CaO-SiO_2-Al_2O_3-ZnO-FeO. This slag system has already been examined extensively by Jak and his co-workers.[12-15] In order to prevent that the used Cu-alloy would be fully oxidized, experiments

are carried out using a partial oxygen pressure of 10^{-7}. In order to work in an industrially relevant temperature frame, a temperature of 1200 °C is chosen.

A methodology has been developed to investigate the behavior of Cu droplets in a slag system towards spinel particles. The interaction of copper towards spinels present in the slag will be examined by decantation of one bigger Cu droplet through the slag system with a well chosen synthetic composition, consisting out of a slag phase and spinel particles. 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. The alumina crucible will react at this interface resulting in the formation of spinel solids. In the first series of experiments, the behaviour of pure Cu droplets in the spinel ($[Fe, Zn]^{2+}[Al, Fe]_2^{3+}O_4$) single-phase region of the slag system, mentioned above, was examined, in order to evaluate the methodology.

A. Thermodynamic calculations

To find an appropriate slag system, factsage is used for thermodynamic calculations, using the FACT53 and FACToxid databases. All componensts of the synthetic slag system are included, namely CaO, SiO_2, FeO, ZnO, Al_2O_3, PbO with addition of Cu. The temperature and the amount of oxygen is assumed to remain constant (1200°C, $p_{O_2} = 10^{-7}$).[16]

A slag composition in the spinel single-phase region has been selected based on thermodynamic calculations. The calculated composition is represented in table 1.

Table 1: Composition for of synthetic slag composition, calculated using Factsage

	ZnO	PbO	SiO_2	Al_2O_3	CaO	FeO
wt%	5	50	11	7	7	20

B. Experiments

a. Melting of the slag composition

All components are weighed and mixed. FeO is added as a combination of metallic iron and hematite, CaO is added as limestone. A protective SiC crucible, containing an Al_2O_3 crucible with the different components mixed, is heated in an inductive furnace (Indutherm) up to a temperature of 800°C, while a protective N_2 atmosphere was established above the slag. At 800°C, the N_2 atmosphere is replaced by a CO/air mixture with volume ratio 1 to 2.44 and a flow rate of 60 l/h, which is preserved during the remaining experiment. The slag is subsequently heated to 1200°C and kept 30 minutes at this temperature in order to melt all components. Subsequently the components are mixed by bubbling N_2 through the liquid mixture for 15 minutes. After an equilibration time of 150 minutes, the molten slag is mixed by bubbling N_2 through the liquid mixture for 5 minutes in order to disperse the solids throughout the slag. After 10 minutes decantation, a sample is taken from the molten slag,

using a cold sampling bar. This slag sample is quenched directly in water. Subsequently the remaining slag is quenched in water using a spoon and dried in a dry chamber at 105°C.

b. Interaction between saturated slag and Cu droplet

Four samples of 30 g were taken from the quenched slag and fed into four separate alumina crucibles (20 ml) and placed in a resistance furnace. The furnace is heated up to a temperature of 800°C, while a protective N_2 atmosphere is set above the slag. At 800°C, the N_2 atmosphere is replaced by a CO/air mixture with volume ratio 1 to 2.44 and a flow rate of 60 l/ h. The furnace is subsequently heated to 1200°C and kept for one hour at this temperature, in order to assure that the slag is completely molten. Subsequently 2.5g Cu is added. After 7, 21 and 42 minutes, a crucible is quenched completely by placing the crucible in water. The fourth crucible is cooled slowly under inert atmosphere (Ar).

C. Analysis methodology

For evaluation of the microstructure, the quenched slag is embedded in epoxy resin and subsequently grinded and polished. The microstructure of the slag is observed using optical microscopy (OM) and secondary electron (SE) imaging using scanning electron microscopy (SEM, Quanta FEG 450). The composition of the present phase is determined using energy dispersive spectroscopy (EDX).

D. Results and discussion

In a first section, the microstructure of the slag system is studied, before addition of the Cu droplets. Subsequently the formation of the spinel layer at the interface between the Al_2O_3 crucible and the slag is discussed. In the next section, the interaction of the Cu droplet with spinel particles in the slag system is discussed and in the last section the methodology is evaluated.

a. Slag system

The microstructure of the slag phase before the addition of the Cu can be observed in Figure 1**.** Two phases can be distinguished: a slag and a spinel phase (25.4 ± 3.4 vol%, white/black faceted solids in OM/SEM images). EDX analyses and compositions are given in Table 2. For the spinel particles, ‘FeO’ is defined as the sum of FeO and ‘FeO’ in Fe_2O_3. The spinel solids are formed from three spinel inducing constituents, namely Al_2O_3, FeO and ZnO. Moreover, the thermodynamic calculated phase equilibrium corresponds nicely with the experimentally obtained results.

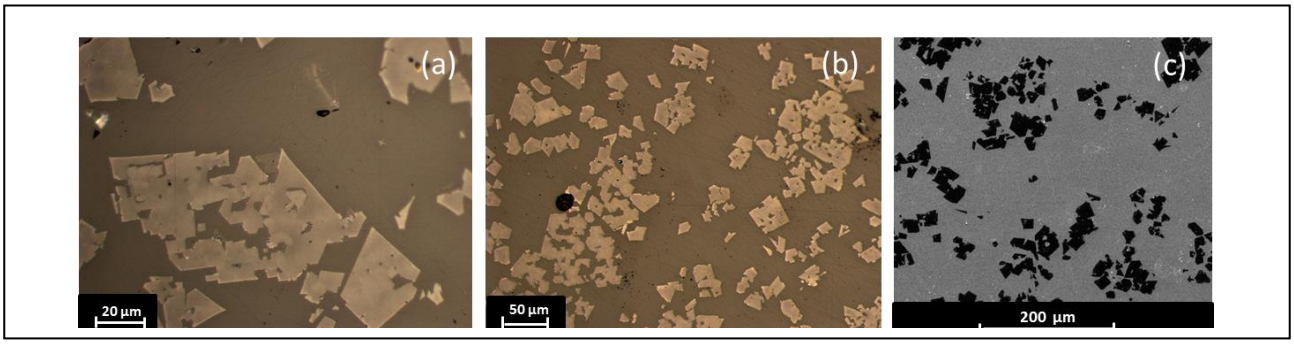

Figure 1: (a) – (b) : OM image of microstructure phase after equilibration – Dark brown phase = slag phase ; light brown particles = spinel particles (c) : SE image of microstructure after equilibration – Light gray phase = slag phase; black particles = spinel particles

Table 2: Composition of slag and spinel solids after equilibration based on EDX analysis

	Al_2O_3	SiO_2	PbO	CaO	'FeO'	ZnO
wt% slag	9.29	25.47	45.69	9.62	6.83	3.06
wt% spinel	41.41	0	0	0	35.77	22.80

b. Evolution of spinel layer at interface with Al_2O_3 crucible

As expected, a spinel layer has formed at the border of the alumina crucible in contact with the slag system was. The evolution of this spinel layer over time is shown in Figure 2.

No well-defined spinel layer has formed after 7 minutes, while after 21 minutes a clear layer was detected of approximately 20 µm. After 42 minutes the layer was approximately 37 µm. EDX analyses were performed on the spinel layers of the crucibles quenched after 21 minutes and 42 minutes, and data are given in Table 2. The composition of the spinel layers is constant with time.

Table 2: Composition of spinel layer of crucibles after equilibration based on EDX analysis

		Al_2O_3	'FeO'	Cu_2O	ZnO
Quenching after 21 min	wt%	42.87	25.61	4.06	27.43
Quenching after 42 min	wt%	46.01	23.58	4.51	25.88

c. Interaction between spinel and liquid Cu

The cross-sections of the quenched crucibles are shown in Figure 3. It can be seen that in the first quenched crucible the Cu droplet bursts out of the slag during quenching. A possible explanation for this observation is the short duration of the experiment which causes only a limited reaction and entrains the Cu droplet occurred yet. After 21 minutes, the Cu droplet was decanted, but had an irregular shape. In time, the shape of the droplet appears to be more and more surface tension driven. The compositions of the quenched slag, spinel particles and

decanted Cu droplet are given in Table 3 and Table 4. It is observed that Cu has dissolved in the slag. A small fraction of Pb has dissolved in the Cu-droplet after 42 minutes.

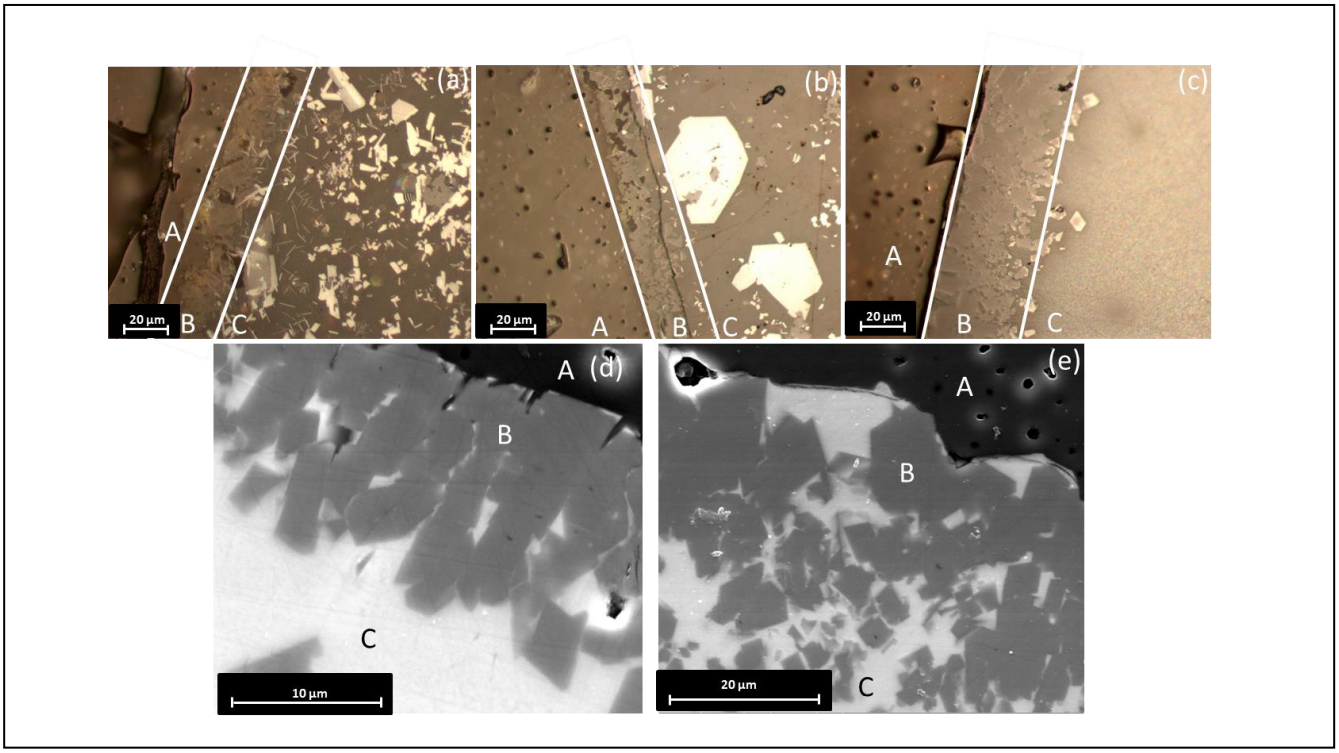

Figure 2: Spinel layer at alumina border. Phase A: Alumina crucible, phase B: spinel border, phase C: slag system (OM images (a) quenched after 7 min (b) quenched after 21 min (c) quenched after 42 min SE images (d) quenched after 21 min (e) quenched after 42 min).

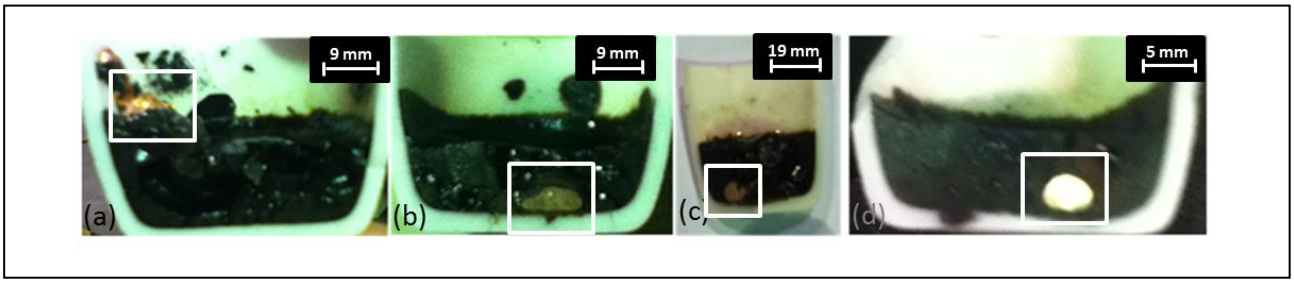

Figure 3: Cross-sections of quenched crucibles after (a) 7 minutes (b) 21 minutes (c) 42 minutes and (d) slowly cooled under protective atmosphere.

Because a spinel layer forms at the bottom of a crucible and by dropping a large Cu particle into the slag, the interaction with the resulting Cu droplet and the spinel layer can be easily visualized. As a result the interaction between a Cu metal droplet and the spinel crystals can be studied while both are in contact with slag.

Table 3: Composition of slag phase and spinel phase in crucibles after quenching based on EDX analysis

	Al_2O_3	SiO_2	PbO	CaO	'FeO'	ZnO	Cu_2O
Quenching after 21 min							
wt% slag	10,75	24.84	37.14	7.79	10.81	0	8.65
wt% spinel	14.20	0	0	0	68.23	17.54	0
Quenching after 42 min							
wt% slag	11.67	21.23	42.25	6.78	8.51	1.24	8.24
wt% spinel	21,48	0	0	0	58.33	16.59	3.57

Table 4: Composition of decanted Cu droplet after quenching based on EDX analysis

	Cu	O	Pb
wt% decanted droplet after 21 min	99.25	0.75	0
wt% decanted droplet after 42 min	99.16	0.68	0.15

Microstructural analysis allows to study the interaction between the spinel particles and Cu. During the persecuted experiments with the simplified slag system and the Cu droplet, it was observed that in none of the crucibles copper droplets stuck to the spinel particles present in the slag. This is different from what is observed in industrial slag systems. Figure 4 shows the microstructure of the crucible quenched after 42 minutes. In the region far from the large decanted Cu droplet, which is on the right-hand side of the figure, no small Cu droplets stick to spinel particles, as illustrated in the detailed microstructure (b). Only in the region near the large Cu droplet, small Cu droplets are observed in the detailed microstructure (c). These small Cu droplets are probably due to the precipitation of dissolved Cu from the slag during too slow quenching. This phenomenon has already been discussed in literature by Genevski and co-workers[17]. Similar observations can be made in the other crucibles. In order to better understand the driving forces for metal droplets to stick to solids, further research is needed.

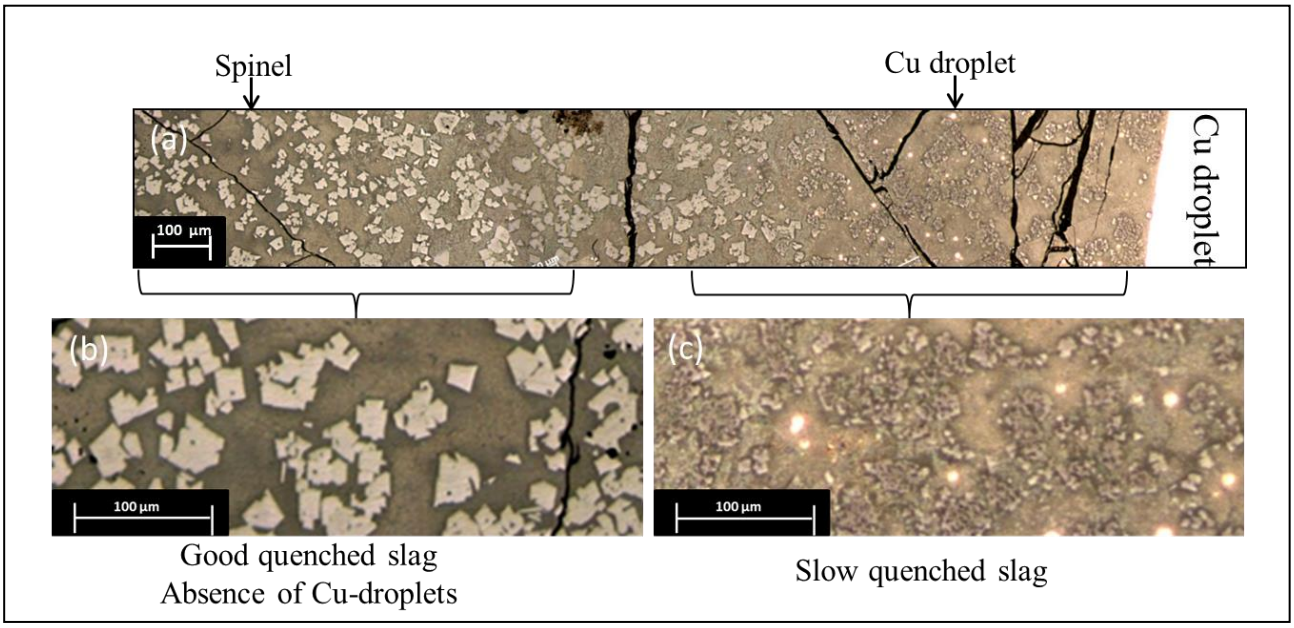

Figure 4: (a) OM image of the microstructure of the crucible quenched after 42 minutes (b) Detail of good quenched microstructure (c) Detail of slow quenched microstructure, close to the decanted Cu droplet

d. Evaluation of the methodology

It can be concluded that the developed experiment setup is suitable to study the interaction between spinel particles and Cu droplets, in a slag matrix. The droplet can be easily visualised in the crucible. Furthermore, the interaction can be evaluated in two possible ways, namely by spinel particles present in the slag, and by the spinel layer at the crucible border.

III. Production of spinel substrates for high temperature contact angle measurements

As at present most studies are performed in absence of slag matrix and in presence of a gas phase, it can be useful to compare to compare the results of the described methodology with results from gas-spinel-droplet experiments as schematically represented in figure 5.

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°C). Consequently standard contact angle measurement equipment cannot be used.

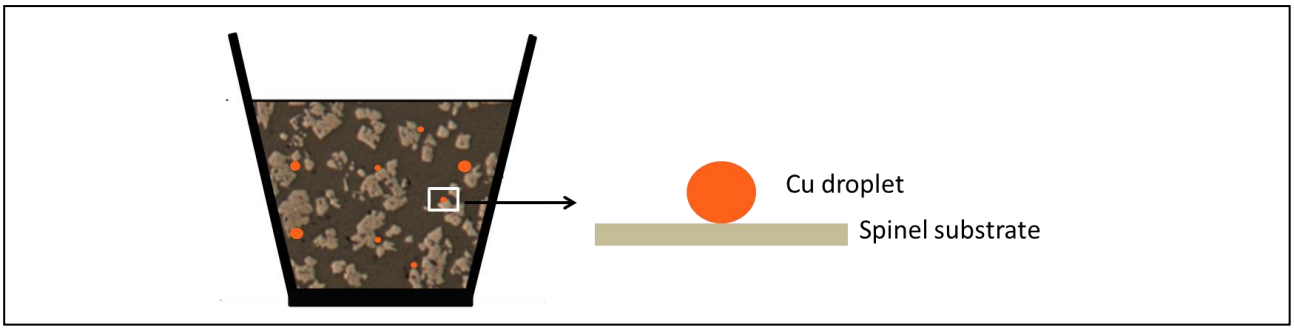

Figure 5: schematic representation of the basic concept of the contact angle measurements

Moreover, 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, Cu alloys have to be produced with a controllable amount of oxygen. As the presence of surface active species such as oxygen and sulphur is very import, the atmosphere has to be selected, controlled and varied carefully. Also the presence of other surface active species has to be avoided to prevent unknown and undesirable effects.

A. Production of spinel substrates

Good substrates for contact angle measurements should be dense, with minimal porosity, chemically homogeneous, free of thermal stresses and produced in a reproducible way. Therefore, a powder metallurgical process was chosen to produce spinel substrates. Two commercially available spinel powders have been selected as the starting material: $MgAl_2O_4$ and Fe_3O_4. Extensive research is available on the production of $MgAl_2O_4$ spinel substrates.[18-21] Magnetite has been selected, as its occurrence in the Cu-production process has been discussed in literature.[4; 22]

a. $MgAl_2O_4$

For the production of $MgAl_2O_4$ substrates, the spark plasma sintering (SPS) equipment is used as described by Vanmeensel and co-workers.[23] A graphite die/punch (inner diameter: 30 mm) set up was filled with dry $MgAl_2O_4$ powder (<50 nm particle size, Sigma Aldrich) and subsequently SPS sintered (type HP D25/1, FCT system Rauenstein, Germany, equipped with a 250 kN uniaxial press) in vacuum for 6 minutes under a load of 60 MPa, applying a heating rate of 200°C/min. The pressure was increased gradually from 5 to 30 MPa at 1050°C within a period of 6 minutes and from 30 to 60 MPa within a period of 3 minutes upon reaching the sintering temperature, as shown in figure 6. After 6 minutes, the current is switched off and followed by a natural cooling, with a cooling rate of about 250°/min. The spark plasma sintered $MgAl_2O_4$ samples were polished using 1-3 µm diamond paste, while a finishing step using colloidal silica (20 nm) was applied.

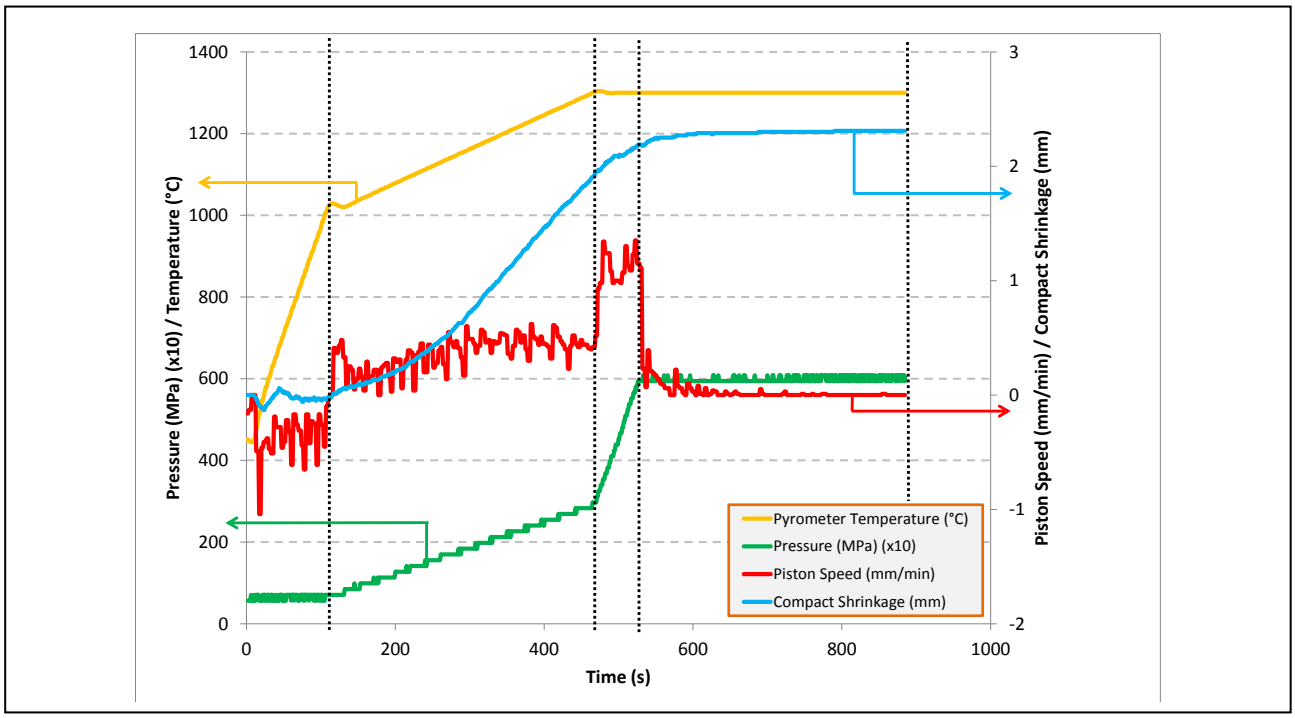

Figure 6: SPS temperature profile determined by a pyrometer focused on the upper punch, SPS pressure profile applied to the sample, SPS piston speed, compact shrinkage of the $MgAl_2O_4$ substrate

Density of the spinel substrate was determined in ethanol at room temperature, using the Archimedes method (BP210S balance, Sartorius AG, Germany). The density of the $MgAl_2O_4$ substrate is 3.5 g/cm³. An XRD diffractometer (Siemens diffractometer D5000) was used for identifying the spinel phase in the SPS sintered substrate. The XRD pattern is shown in figure 7. All of the diffraction peaks can be indexed to the cubic spinel structure of $MgAl_2O_4$ (International centre for diffraction data, No 00-021-1152). This indicates that the SPS sintering does not have an influence on the chemical composition of the $MgAl_2O_4$.

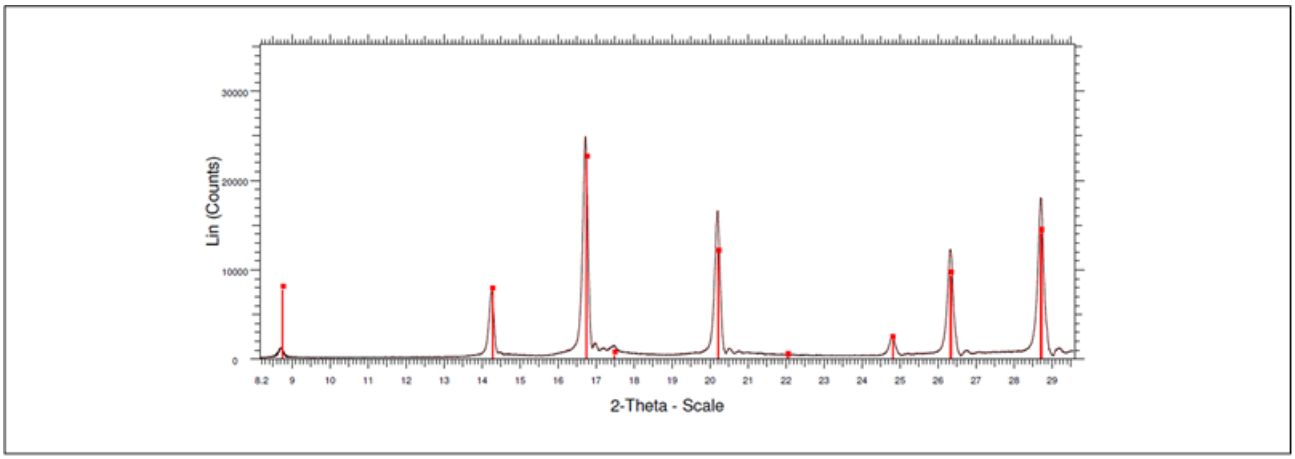

Figure 7: XRD pattern of $MgAl_2O_4$ substrate obtained by SPS sintering, and reference diffraction peaks (red) of $MgAl_2O_4$ (International centre for diffraction data, No 00-021-1152)

Five Vickers hardness indentations were made on the polished surfaces, applying an indentation load of 10 kg (FV-700 Vickers hardness indenter, Future-Tech Corp., Tokyo, Japan). The fracture toughness of the SPS processed materials was calculated from the crack lengths protruding from the edges of the hardness indentations. The Anstis formula was used to calculate the fracture toughness values[24]:

$$K_{1C} = 0.016\left(\frac{E}{H_V}\right)^{1/2} \times \frac{F}{c^{3/2}}$$

with E the Young's modulus, estimated at 280 GPa , H_V the Vickers hardness (GPa), F the applied indentation force (N) and c the crack length from the center of the indent to the crack tip (m). An average Vickers hardness and fracture toughness of HV-10kg of 13.8 ± 0.5 GPa and K_{1C} = 1.5 ± 0.1 MPa.m1/2, respectively, were obtained, in good agreement with earlier reported values.[25; 26] Representative optical micrographs of the polished $MgAl_2O_4$ microstructure as well as 10 kg indentations are shown in Figure 8.

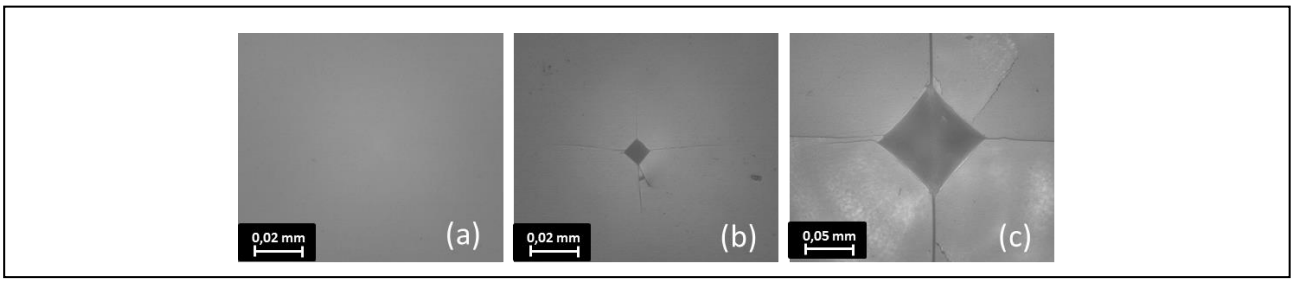

Figure 8: Representative optical micrograph of the polished $MgAl_2O_4$ sample surface (a) and Vickers hardness indentations, with protruding cracks located at the indenter tips (b-c).

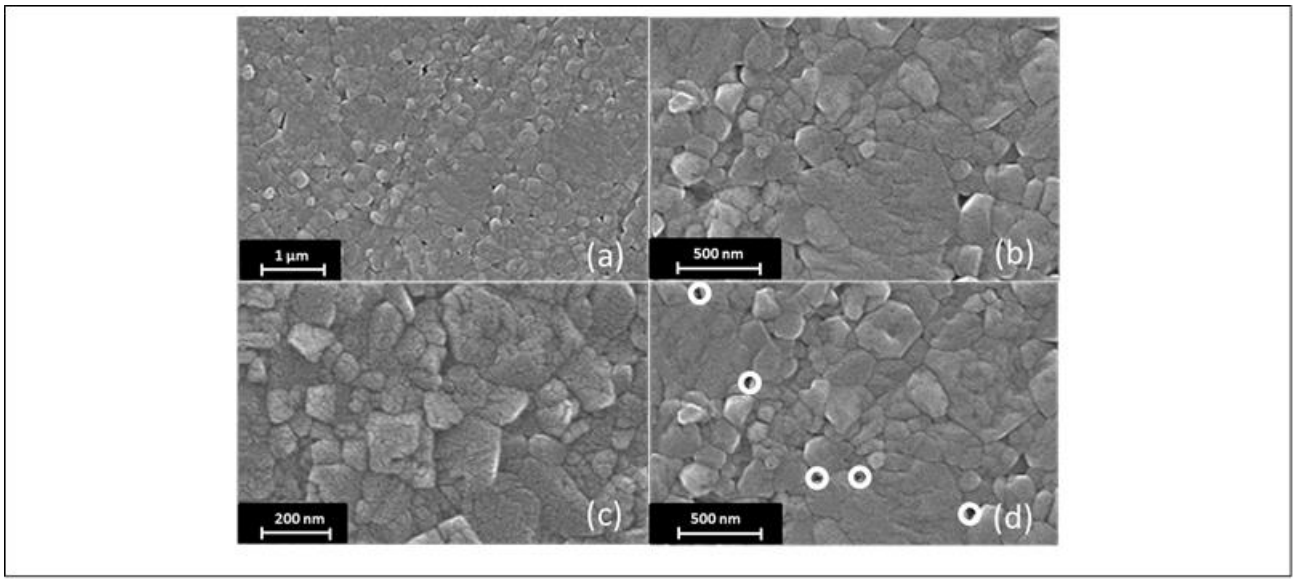

Figure 9: Representative secondary SE image of polished and thermally etched $MgAl_2O_4$ sample surfaces. The white circles in Figure (d) indicate the presence of closed pores at the triple junctions between the different grains.

The polished $MgAl_2O_4$ samples were thermally etched in air at 1200°C during 30 minutes (Nabertherm HT 16/17, Lilienthal, Germany), i.e. 100°C below the sintering temperature in order to avoid excessive grain growth by grain boundary migration. Scanning electron microscopy (SEM) was performed at 20 kV using a secondary electron detector (Philips XL 30 FEG, Eindhoven, The Netherlands). A Au-Pt layer was sputtered on the samples. The secondary electron (SE) images (Figure 9 (a)-(d)) indicate that thermal etching was successful in revealing the grain boundaries in the polycrystalline material. Furthermore, a fine microstructure with a limited amount of pores, as indicated in (d), was obtained, indicating that SPS is capable of maintaining the intrinsic nanostructure of the powder, while enhancing the densification process. The majority of the grains have grain sizes ranging between 50 and 500 nm, while local coarsening resulted in a limited amount of coarser grains with an average size of 1 µm. The shown microstructures clearly indicate that only isolated pores are present at the triple junctions between the distinct grains, confirming that open porosity is absent and guaranteeing that liquid Cu will not penetrate the spinel phase. Finally, it is expected that the fine microstructure and reduced porosity level will contribute to improved mechanical and functional properties such as bending strength and thermal shock resistance.

b. Fe_3O_4

Magnetite powder has been purchased (< 5 µm, 95%, Sigma Aldrich) and free sintering has been applied. The powder has first been compressed into pellets and subsequently sintered. Different combinations of compression pressures and sintering conditions were tested. However, in each case, difficulties have been experienced with the physical properties and the chemical composition of the substrates.

The main difficulties with respect to the physical properties were the occurrence of deformations, due to thermal stresses originating from the production process. The presence of these thermal stresses became visible during contact angle measurements performed on the produced substrates. The chemical instability of magnetite under the different sintering atmosphere also appeared to be inevitable, leading to the formation of a certain amount of hematite or wustite, as was confirmed by XRD measurements. This observation was related to the fact that there is only a restricted range of the partial oxygen pressures where magnetite is stable, as was for example described by Yang and co-workers. [27]

IV. Conclusions

A suitable methodology has been developed to investigate the interaction between Cu droplets and spinel particles in the presence of a slag system, which has been confirmed by the first experiments, persecuted using a synthetic slag system with a composition in the spinel single phase region of the slag and pure copper. A comparison of this methodology with the interaction between spinel substrates and Cu in the presence of a gas phase, using high temperature contact angle measurements, could be very useful. A reliable and reproducible

methodology has been developed for the production of $MgAl_2O_4$ spinel substrates, which will subsequently be used in high temperature contact angle measurements.

Acknowledgements

The authors wish to thank the agency for innovation by science and technology in Flanders (IWT, project 110541) and Umicore for its financial support. In particular Maurits Van Camp, Luc Coeck, Saskia Bodvin, Kristel Van Ostaeyen, Eddy Boydens, Ann Van Gool and the technical staff of Umicore R&D are thanked for their support with the experiments and characterization. K. Vanmeensel wants to thank the Research Fund Flanders (FWO) for his postdoctoral Fellowship. Greetje Godier from Flamac is thanked for the help for the XRD measurements.

References

[1] IN-KOOK S., WASEDA Y, YAZAWA A., (1988): Some interesting aspects of non-ferrous metallurgical slags. High Temperature Materials and Processes **8:** 65-88.

[2] LIOW, J. L., JUUSELA M. , GRAY N.B. and SUTALO I.D. , (2003): Entrainment of a two-layer liquid through a taphole. Metallurgical and Materials Transactions B-Process Metallurgy and Materials Processing Science **34:** 821-832.

[3] CARDONA N., Hernandez L., Araneda E, PARRA R., (2010): Evaluation of copper losses in the slag cleaning circuits from two Chilean smelters, pp. in *Proceedings of Copper*.

[4] IMRIS, I., S. REBOLLEDO, M. SANCHEZ, G. CASTRO, G. ACHURRA *et al.*, (2000): The copper losses in the slags from the El Teniente process. Canadian Metallurgical Quarterly **39:** 281-289.

[5] SRIDHAR, R., J. TOGURI and S. SIMEONOV, (1997): Copper losses and thermodynamic considerations in copper smelting. Metallurgical and Materials transactions B **28:** 191-200.

[6] CARDONA, N., P. COURSOL, P. J. MACKEY and R. PARRA, (2011): Physical chemistry of copper smelting slags and copper losses at the Paipote smelter Part 1-Thermodynamic modelling. Canadian Metallurgical Quarterly **50:** 318-329.

[7] JONG-LENG, L., M. JUUSELA, N. B. GRAY and I. D. SUTALO, (2003): Entrainment of a two-layer liquid through a taphole. Metallurgical and Materials Transactions B (Process Metallurgy and Materials Processing Science) **34B:** 821-832.

[8] MARUYAMA T., FURUI N. , HAMAMOTO M. and SUNAMOTO T., (2003): The copper loss in slag of flash smelting furnace in Tamano smelter. Yazawa international Metallurgical and materials processing: principles and technologies vol II : high-temperature metals production

[9] IP, S. W., and J. M. TOGURI, (1992): Entrainment behavior of copper an copper matte in copper smelitng operations. Metallurgical Transactions B-Process Metallurgy **23:** 303-311.

[10] MINTO, R., and DAVENPOR.WG, (1972): Entrapment and flotation of matte in molten slags : GS. Canadian Mining and Metallurgical Bulletin **65:** 70-&.

[11] MARU, H. C., D. T. WASAN and R. C. KINTNER, (1971): Behaviour of a rigid sphere at a liquid-liquid interface. Chemical Engineering Science **26:** 1615-&.

[12] JAK, E., and P. C. HAYES, (2003): The effect of the CaO/SiO2 ratio on the phase equilibria in the ZnO-"Fe2O3"-(PbO+CaO+SiO2) system in air: CaO/SiO2=0.1, PbO/(CaO+SiO2)=6.2, and CaO/SiO2=0.6, PbO/(CaO+SiO2)=4.3. Metallurgical and Materials Transactions B-Process Metallurgy and Materials Processing Science **34:** 369-382.

[13] JAK, E., B. J. ZHAO, I. HARVEY and P. C. HAYES, (2003): Experimental study of phase equilibria in the PbO-ZnO-"Fe(2)O(3)"-(CaO+SiO(2)) system in air for the lead and zinc blast furnace sinters (CaO/SiO(2) weight ratio of 0.933 and PbO/(CaO+SiO(2)) ratios of 2.0 and 3.2). Metallurgical and Materials Transactions B-Process Metallurgy and Materials Processing Science **34:** 383-397.

[14] JAK, E., and P. C. HAYES, (2002) Experimental liquidus in the PbO-ZnO-"Fe2O3"-(CaO+SiO2) system in air, with CaO/SiO2=0.35 and PbO/(CaO+SiO2)=3.2. Metallurgical and Materials Transactions B-Process Metallurgy and Materials Processing Science **33:** 851-863.

[15] JAK, E., and P. C. HAYES, (2002) Experimental study of phase equilibria in the PbO-ZnO-"Fe2O3"-CaO-SiO2 system in air for high lead smelting slags (CaO/SiO2=0.35 and PbO/(CaO+SiO2)=5.0 by weight). Metallurgical and Materials Transactions B-Process Metallurgy and Materials Processing Science **33:** 817-825.

[16] CAMPFORTS, M., K. VERSCHEURE, E. BOYDENS, T. VAN ROMPAEY, B. BLANPAIN *et al.*, (2007): On the microstructure of a freeze lining of an industrial nonferrous slag. Metallurgical and Materials Transactions B-Process Metallurgy and Materials Processing Science **38:** 841-851.

[17] GENEVSKI, K., and V. STEFANOVA, (2008) Dispersed matte droplets in industrial slag melts from flash smelting furnace. Canadian Metallurgical Quarterly **47:** 51-58.

[18] BONNEFONT, G., G. FANTOZZI, S. TROMBERT and L. BONNEAU, (2012): Fine-grained transparent MgAl2O4 spinel obtained by spark plasma sintering of commercially available nanopowders. Ceramics International **38:** 131-140.

[19] WANG, C., and Z. ZHAO, (2009): Transparent MgAl2O4 ceramic produced by spark plasma sintering. Scripta Materialia **61:** 193-196.

[20] MORITA, K., B. N. KIM, K. HIRAGA and H. YOSHIDA, (2008): Fabrication of transparent MgAl2O4 spinel polycrystal by spark plasma sintering processing. Scripta Materialia **58:** 1114-1117.

[21] FRAGE, N., S. COHEN, S. MEIR, S. KALABUKHOV and M. P. DARIEL, (2007): Spark plasma sintering (SPS) of transparent magnesium-aluminate spinel. Journal of Materials Science **42:** 3273-3275.

[22] YAZAWA, A., (1974): Thermodynamic considerations of copper smelting. Canadian Metallurgical Quarterly **13:** 443-453.

[23] VANMEENSEL, K., A. LAPTEV, O. VAN DER BIEST and J. VLEUGELS, (2007): The influence of percolation during pulsed electric current sintering of ZrO2-TiN powder compacts with varying TiN content. Acta Materialia **55:** 1801-1811.

[24] ANSTIS, G. R., P. CHANTIKUL, B. R. LAWN and D. B. MARSHALL, (1981): A CRITICAL-EVALUATION OF INDENTATION TECHNIQUES FOR MEASURING FRACTURE-TOUGHNESS .1. DIRECT CRACK MEASUREMENTS. Journal of the American Ceramic Society **64:** 533-538.

[25] SUTORIK, A. C., G. GILDE, J. J. SWAB, C. COOPER, R. GAMBLE *et al.*, (2012): The Production of Transparent MgAl2O4 Ceramic Using Calcined Powder Mixtures of Mg(OH)2 and gamma-Al2O3 or AlOOH. International Journal of Applied Ceramic Technology **9:** 575-587.

[26] GOLDSTEIN, A., A. GOLDENBERG, Y. YESHURUN and M. HEFETZ, (2008): Transparent MgAl2O4 Spinel from a Powder Prepared by Flame Spray Pyrolysis. Journal of the American Ceramic Society **91:** 4141-4144.

[27] YANG, L. X., and E. MATTHEWS, (1997): Sintering reactions of magnetite concentrates under various atmospheres. Isij International **37:** 1057-1065.