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Sessile drop evaluation of high temperature copper/spinel and slag/spinel interactions

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Abstract: Metal droplets sticking to spinel solids, present in metallurgical slag systems, play an important role in hindering the sedimentation of copper in slags. To understand this phenomenon, the interaction between spinel particles with Cu on one hand and with slag, on the other hand, was evaluated. A dedicated approach was applied, using an industrially relevant synthetic slag system $PbO-FeO-SiO_2-CaO-Al_2O_3-Cu_2O-ZnO$, pure copper and $MgAl_2O_4$ substrates to represent the industrial slag, the entrained copper droplets and the spinel solids, respectively. Both the copper−$MgAl_2O_4$ and the slag−$MgAl_2O_4$ interaction were studied using sessile drop measurements, combined with an extensive microstructural analysis. Additionally, the effect of time on the slag−$MgAl_2O_4$ interaction was studied using immersion experiments. Copper displayed a non-wetting behaviour on $MgAl_2O_4$, whereas slag displayed a reactive wetting and an interaction layer of $(Mg,Fe,Zn)(Al,Fe)_2O_4$ spinel was formed at the interface, which was also observed in the immersion experiments. Moreover, the diffusion of MgO and Al_2O_3 from the spinel substrate into the slag droplets was noted.
Key words: sessile drop; copper; spinel; slag

1 Introduction

Slags play an essential role in pyrometallurgical processes, for the elimination of unwanted impurities or acting as collectors for specific groups of metals. Therefore, a decantation step is often used in pyrometallurgical processes, allowing the phase separation between matte or metal and slag. Although desirable, these phase separations are not perfect, therefore industrial copper plants suffer from metal losses in slags, which confines the overall metal recovery [1]. To minimize these metal losses and improve the efficiencies of the industrial plants, it is essential to determine the origin and mechanisms behind these metal losses.

Based on extensive research performed on copper losses, it is currently well accepted that copper losses in slags are attributed to both mechanical entrainment of copper-containing droplets and chemical copper losses [2−4]. Chemical copper losses are caused by the dissolution of copper as sulphide and oxide for primary copper production and mainly in its oxide form for secondary copper production. This type of losses is intrinsic to pyrometallurgical processes and is determined by the thermodynamic parameters of the system such as the temperature, the composition of the slag and the matte phase [3,5−7], the oxygen partial pressure [3,5−7], the kinetics and the chemical activity of the metal [3].

Mechanically entrained copper is defined as entrapped or floating unsettled droplets. In primary copper production, both matte and metallic droplets occur, while in secondary copper production, these losses are mainly under the form of metallic copper droplets. Mechanically entrained droplets are ascribed to a variety of causes. The first important cause is the dispersion of copper sulphide or copper, which precipitates due to a local change of the solubility in the slag, for example, in zones with different oxygen partial pressures or a lower

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temperature due to inhomogeneity of the process [8]. The second important source is entrained matte or metal, originating from gas-producing reactions dispersing metal into the slag. The resulting SO_2 bubbles nucleate at the bottom of the furnace and can elevate a surface film of matte or metal to the slag above [8−10]. Mechanical losses can also occur from operational procedures typically performed in pyrometallurgical processes like tapping or charging. Mechanical entrainment during tapping can originate due to the rise of a denser layer, which can happen while flowing around obstructions in the vessel [2]. The physical dispersion of matte or metal into the slag by mixing can originate from several causes such as gas injections, pouring one phase into the other or the presence of turbulence [2,11]. The above-mentioned sources have been examined profoundly and reported in literature. Additionally, the penetration of metallic copper into refractory can lead to metal losses [12]. There is, however, the fifth possible cause of mechanically entrained metal droplets, namely the attachment of droplets to solids in the slag, which obstructs their decantation. In copper industry, these solids are often identified to have a spinel structure. Notwithstanding the fact that the phenomenon has been reported by IP and TOGURI [8] and ANDREWS [11], and was observed by DE WILDE et al [13], so far limited industrial or experimental data concerning this phenomenon were reported. A prerequisite to further improve the phase separation in pyrometallurgical processes is a better understanding of the interactions among the three different phases involved (metal droplet, solids and slag).

Different methodologies have been applied to studying metal losses in slags. However, little attention has been given to the phenomenon of sticking droplets and more specifically to the spinel–copper and spinel–slag interactions. The wetting behaviour between metals and oxides has been studied frequently, as summarized by EUSTATHOPOULOS and DREVET [14]. In most cases, a distinction is made between reactive and non-reactive systems. Non-reactive systems reach equilibrium in less than 0.1 s for millimetre sized droplets while slower spreading kinetics is a strong indication of the presence of interfacial reactions [15−17]. With respect to the specific wettability of metals on spinel substrates, KOZLOVA and SUVOROV [18] and FUKAMI et al [19] performed experimental studies on the wettability of iron on $MgAl_2O_4$ spinel substrates, but no data have been found on the wetting of copper on spinel substrates specifically.

Wettability between slags and spinels has been studied in the frame of the study of inclusion removal in steel refining on one hand, and the effect of the slag attack on refractories on the other hand. ABDEYZDAN et al [20] investigated the wettability of $CaO-Al_2O_3-SiO_2-MgO$ slag on $MgAl_2O_4$ spinels, and concluded that the slag showed a fast decrease of the contact angle during the first second, after which a plateau is reached for longer time [20]. Even at shorter timescales, slag reaction and penetration were observed. DONALD et al [21] studied the interactions between fayalite slags and synthetic spinels, representing refractory materials. Interfacial reaction products and dissolution of various refractory compounds into the slags were observed. TRAN et al [22] studied the wetting between magnesia spinel bonded refractory and slag, revealing the effect of the Fe-content in the slag and temperature. Nevertheless, previous research focused on fayalite-type slags. Studies on the wetting behaviour between spinel and PbO-based slag have, to our knowledge, not been published before. Moreover, the sessile drop technique was not used before studying the losses due to the attachment of copper droplets to spinel solids in a slag phase.

This present study focuses on the interaction between spinel substrates and slag or copper, respectively. In this research, $MgAl_2O_4$ was chosen to represent the spinel phase, as this is one of the most stable spinel powders. A synthetic industrially relevant PbO-based slag was used ($PbO-FeO-SiO_2-CaO-Al_2O_3-Cu_2O-ZnO$). The (dynamic) wetting behaviour of spinel/copper and spinel/slag has been investigated combined with a detailed microstructural analysis. In addition, the evolution in time of the interaction between spinel and slag has been studied by variation of the immersion time of spinel substrates in the slag.

2 Experimental

2.1 Production of slag system

The slag was produced by melting oxides of appropriate quantities. Therefore, an appropriate slag composition was selected to obtain a spinel saturated single phase slag based on thermodynamic calculations using FactSage 6.4 thermochemical package (FACT and FT Oxid database). The final targeted slag composition is shown in Table 1. CaO was added as limestone and FeO was added as a combination of metallic iron and hematite. 400 g of the targeted composition was weighed, mixed and transferred in an Al_2O_3 crucible (270 mL). The Al_2O_3 crucible, surrounded by a protective SiC crucible, was heated in an inductive furnace (Indutherm, MU3000) 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 was replaced by CO/air mixture with a volume ratio of 1 to 2.44, corresponding to an oxygen partial pressure (p_{O_2}) of 10^{-2} Pa, with a total flow rate of 60 L/h, which was kept constant during the remainder of the experiment.