Electrocapillary Phenomena in Molten Metal-Slag Systems

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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]:

\[
-d\sigma = \varepsilon \cdot d\varphi + \sum_i \Gamma_i \cdot d\mu_i ,
\]

(1)

where \( \varphi \) is the electric (electrode) potential of metal, \( \Gamma_i \) is adsorption (excess concentration) of a component \( i \) at the interface and \( \mu_k \) 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-alumino-silicate 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.

![ECC graphs](image)

**Figure 1:** ECC of copper at 1410°C (left) and iron at 1550°C (right) in slag (mass.%) 40 CaO, 40 SiO$_2$, 20 Al$_2$O$_3$ [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.

![Electrocapillary effects](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


