Modeling electrochemical transport of ions in the ESR process

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Abstract

Numerous electrochemical reactions were suggested for chemical elements such as S, O, Al, and Fe to describe metal refinement mechanisms in the ESR. Electrochemical (Faradaic) reactions take place at slag-metal-gas-mold interfaces. Specifically, those reactions are carried out at the liquid film under the electrode tip as well as at the droplet-slag interface. We propose a model for Faradaic reactions at those interfaces as well as electrochemical transport of ions in the bulk of slag. It is found that the intensity of the flow filed and the strength of electric field in the bulk of slag can significantly impact Faradaic reactions and consequently efficiency of metal refinement. Impacts of electrode polarity and electro-migration of ions are analyzed. Based on modeling results some explanations are suggested for theses phenomena in DC ESR: relationship between melt rate and polarity of electrode, and formation of FeO layer under electrode tip.

Introduction

In ESR process, several electrochemical (Faradaic) reactions take place at the slag-metal interface aiming at obtaining an alloy which is as cleaned and chemically refined as possible. For instance, Faradaic reactions of alloying elements such as Ti, S, and Al were reported [1]. The melt rate of the ESR electrode with positive polarity (anodic) was observed in-situ to be higher than that for the ESR electrode with negative polarity (cathodic) during DC operation of the process [2]. Mitchell et al [3] reported the formation of a thick layer of iron oxide (FeO) under the tip of electrode (not the lateral wall) during the experiment. FeO formation requires the presence of an excessive amount of O^{2-} near the anodic electrode where an enormous amount of Fe^{2+} is injected into the slag. Apparently, the aforementioned phenomena are attributed to the ionic properties of the molten slag. Thereby, a dominantly ionic mechanism for the conduction of the electric current was noticed [4].

In this paper, we carry out numerical simulations to explore possible explanations for the aforementioned phenomena namely higher melt rate for the electrode with positive polarity and formation of a thick layer of FeO at the tip of ESR electrode operating under DC voltage.

Modeling

Here, the CaF_2-based slag (electrolyte) is assumed to be fully dissociated into its component ions including Ca^{2+}, F^-, O^{2-}, and Fe^{2+}. The electrochemical transports of ions are modeled by solving Poisson–Nernst–Planck (PNP) equations that includes advection, diffusion, and electro-migration of ions. The model accounts for the Faradaic reaction at slag-metal interface through Butler-Volmer formula. Details of the model are presented in Refs. [5-8].

Results and discussions

Phenomenon 1: The relationship between the electrode melt rate and polarity

Fig. 1 illustrates the calculated distribution of current density in the bulk of slag for three cases considering different polarity for the electrode and different applied voltage. The highest amount of current density (J_{max}) is observed under the edge of electrode, whereas a very low current density flows near the upper edge of the domain (mold-slag-air interfaces). At a steady state, the current density is determined by the flux of the reacting ferrous ion (Fe^{2+}) that in turn is dependent on the voltage and electrode polarity. As shown in Fig. 1 (a) and Figure 1 (b), either a semicircular profile or a dumbbell-shaped profile of the current density may develop by altering the polarity of the electrode from positive (anodic) to negative (cathodic), respectively. The parabolic profile is obtained as the voltage increases, as shown in Figure 1 (c). The obtained results reveal that Ohm's law is not valid in the bulk of the slag with non-uniform ionic concentrations. Generally, the distribution of Joule heating significantly impacts the thermal field in the slag. The amount of released Joule heat to the slag correlates with the current density. Obviously, the amount of current density (~ Joule heating) is much greater near the electrode with the positive polarity compared to that of the negative polarity comparing Fig. 1 (a) and Fig.

1 (b). The aforementioned findings can well explain the in-situ observation of higher melt rates for an anodic ESR electrode (positive polarity) than the cathodic one (negative polarity) in the DC-operated ESR process [2]. Details of this study are available in Ref. [7].

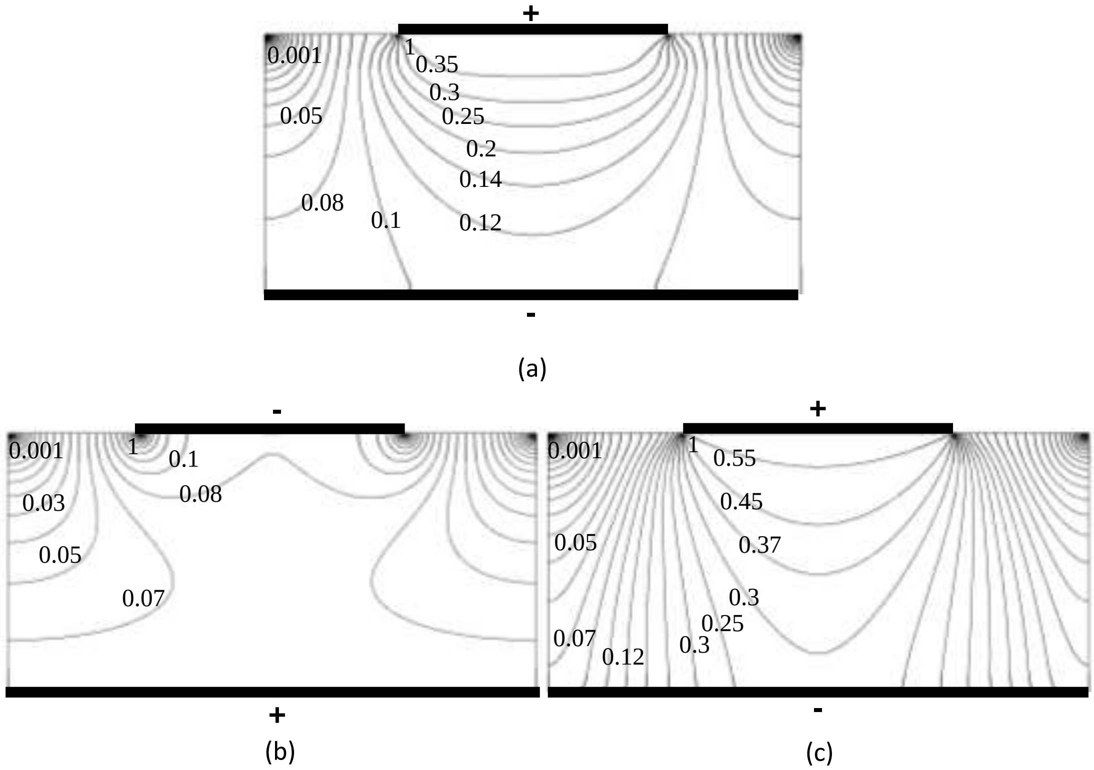


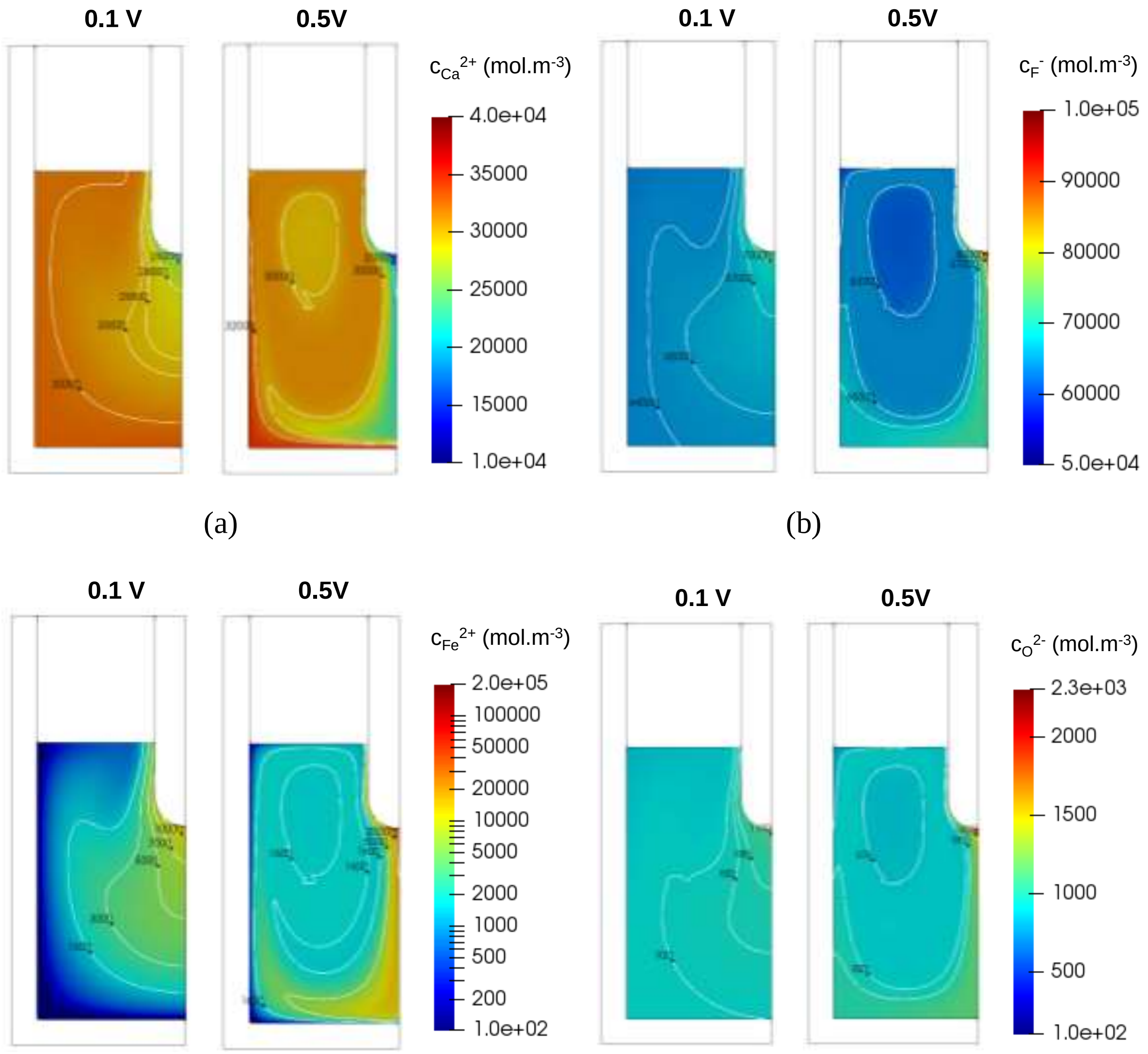
Fig. 1. Distributions of the magnitude of electric current density are shown within the slag of ESR process for three cases. In all cases the maximum current density (J_{max}) is under the edge of electrode. Isolines of the current density are labeled using the normalized current density (J/J_{max}). (a) Positive polarity for the electrode (J_{max}=850 A.m^{-2}); (b) Negative polarity for the electrode (J_{max}=850 A.m^{2}); (c) Positive polarity for the electrode (J_{max}=2500 A.m^{-2}).

Phenomenon 2: The formation of a thick layer of FeO under the tip of electrode

Mitchell et al [3] conducted several experiments using the galvanostatic pulsing technique to measure the magnitude of overpotential that arises from concentration polarization at the interface between the pure iron electrode and CaF_2-based slags. Here, the numerical model is configured according to this experiment.

As an example, the calculated concentration fields for all ions (Ca^{2+}, F^{-}, Fe^{2+}, and O^{2-}) under different applied voltages are illustrated in Fig. 2. As anticipated, anions (F^{-} and O^{2-}) move toward the anode, and inert cation (Ca^{2+}) accumulates adjacent to the cathode. The migration flux occurs in a direction opposite to the advection flux for anions; hence, they compete against each other. In contrast, migration and advection follow the same route, thus assisting in the transport of cations (Ca^{2+} and Fe^{2+}) toward the cathodic crucible. As shown in Fig. 2 (a), the distribution of Ca^{2+} is non-uniform along the crucible wall at a large applied voltage. The concentration of Ca^{2+} is relatively low at the cathodic crucible near the free surface of the slag where the electric current density is high. In the absence of sufficient Fe^{2+}, the electric current is delivered from the slag to the cathode by the Faradaic reaction of Ca^{2+}. As a result, Ca^{2+} is not uniformly consumed at the surface of the cathode where the distribution of electric current density is non-uniform. As shown in Fig. 2 (c), the concentration of Fe^{2+} is remarkably high near/at the anodic electrode-slag interface where the Fe^{2+} is continuously injected into the slag. In contrast, a region of low Fe^{2+} concentration appears along the crucible where intense removal of ferrous ion occurs. Despite the opposition between the advection and migration, a significant amount of anions can accumulate under the tip of anodic electrode. This finding implies that the migration flux surpasses the advection flux of anions near the tip of electrode where a strong electric field/electric current density exists. Furthermore, the well-known severe recirculation of flow in the bulk of slag notably influences the concentration fields of all ions especially near the vortex core. The concentration fields for all involving ions remain non-uniform although a significant amount of current density (order of 10^5 $A.m^{-2}$) flows through the well-mixed slag ($u \sim 2$ $mm.s^{-1}$). In other words, the presence of an intense electro-vortex flow cannot guarantee a uniform concentration field for ions.

As previously described, the strong advection flux opposes the migration flux for anions (e.g., O^{2-}) near the electrode. Therefore, a significant amount of O^{2-} must be washed away from the electrode surface by the flow. To propose a possible explanation for the aforementioned phenomenon, magnitudes of advection flux, $\left\| \vec{u} c_{O^{2-}} \right\|$, diffusion flux, $\left\| D_{O^{2-}} \vec{\nabla} c_{O^{2-}} \right\|$, and migration flux, $\left\| \frac{D_{O^{2-}}}{RT} F z_{O^{2-}} c_{O^{2-}} \vec{\nabla} \varphi \right\|$, for O^{2-} along the surface of electrode and axis of slag are plotted as shown in Fig. 3. The advection and migration exhibit relatively similar strength near the lateral wall. However, the migration defeats the advection in the region near the tip of electrode where the electric field (current density) is large. The magnitude of velocity is notably small in the vicinity of electrode tip as illustrated in Fig. 3. Therefore, a massive amount of O^{2-} can reach the tip of electrode to participate in a chemical reaction with Fe^{2+}. The aforementioned finding can explain the in situ observation of the formation of a thick FeO layer under the tip of electrode [3]. Details of this study are available in Ref. [8].



(a) (b)

(b) (d)

Fig. 2. The calculated concentration fields of all involved ions in the slag (left contour) low applied voltage (Vapp= 0.1 V) and (right contour) high applied voltage (Vapp= 0.5 V) are compared: (a) concertation field of Ca^{2+}, (b) concertation field of F^{-}, (c) concertation field of Fe^{2+} (logarithmic scale), (d) concertation field of O^{2-}. In all contours, iso-lines of concentrations are also inserted.

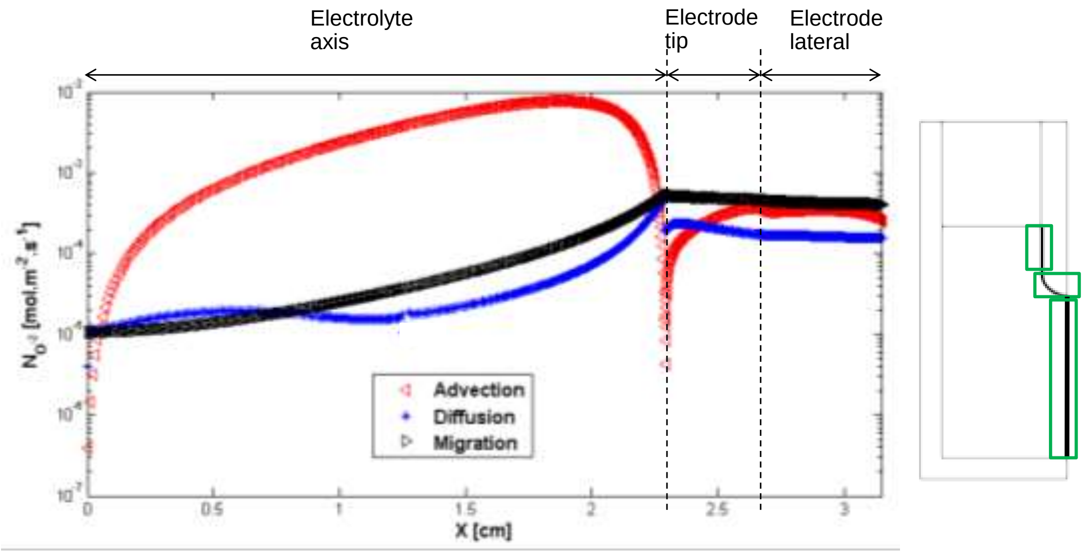


Fig. 3. Advection, diffusion, and migration fluxes of $O^{2-}$are plotted along the electrode surface (lateral wall and tip) and the axis of slag.

Summary

In this paper, we carry out numerical simulations to explore possible explanations for two phenomena namely higher melt rate for the electrode with positive polarity compared to that with negative polarity, and formation of a thick layer of FeO at the tip of ESR electrode operating under DC voltage. Here, a fully dissociated CaF_2-based slag is modeled including Ca^{2+}, F^{-}, O^{2-}, and Fe^{2+} ions. The electrochemical transports of ions are modeled by solving Poisson–Nernst–Planck (PNP) equations that includes advection, diffusion, and electro-migration of ions. The model takes into account Faradaic reaction of ferrous ion Fe^{2+} at slag-metal interface through Butler-Volmer formula. The variations in concentration overpotential and distribution of electric current density related to the polarity of electrode explain the relationship between melt rate and polarity of electrode. The strong electro-migration of O^{2-} attributes the formation of FeO layer under the electrode in DC operated ESR process.

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