Electrochemical Behavior of Ni2+ in SiO2-CaO-MgO-Al2O3 Molten Slag at 1673 K (Postprint)

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Abstract

A controlled oxygen flow electrolytic cell with Pt, O2(air)|ZrO2 as the reference electrode was integrally constructed using an MgO-partially-stabilized ZrO2 solid electrolyte tube. The electrochemical behavior of Ni2+ in SiO2-CaO-MgO-Al2O3 molten slag at 1673 K was investigated using electrochemical techniques including cyclic voltammetry, square wave voltammetry, chronopotentiometry, and constant-potential electrolysis. The results demonstrate that diffusion of O2- in the molten slag and its electromigration within the ZrO2 solid electrolyte are not the rate-limiting steps for reduction of electroactive species in the slag, and that investigation of the electrochemical behavior of Ni2+ in molten slag using the constructed controlled oxygen flow electrolytic cell is feasible under the present experimental conditions. The reduction of Ni2+ to Ni on an Ir electrode in molten slag is a reversible, one-step, diffusion-controlled reduction process. The diffusion coefficients of Ni2+ in slag containing 3% NiO were calculated to be (3.50$±0.18)×10 $-6 and$ (2.80±0.22)×$10-6 cm2/s from data obtained by cyclic voltammetry and chronopotentiometry, respectively, which are in good agreement with literature values.

Full Text

Electrochemical Behavior of Ni^{2+} in SiO_2-CaO-MgO-Al_2O_3 Molten Slag at 1673 K

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Abstract

The modern iron and steel industry produces large emissions of CO_2 annually. Electrolytic reduction of molten slag containing iron oxide at high temperature using an inert oxygen-evolving anode represents an alternative process that could reduce or eliminate CO_2 formation. To establish reasonable process parameters for electrolytic production of Ni-containing steel, it is necessary to understand the electrochemical behavior of Ni^{2+} in molten slag. However, investigations on the electrochemical behavior of Ni^{2+} in molten slag at elevated temperatures have been very limited, likely due to experimental difficulties associated with operating high-temperature electrochemical cells.

In this work, an electrolytic cell with controlled oxygen flow was constructed integrally using a one-end-closed magnesia partially stabilized ZrO_2 (MSZ) solid electrolyte tube, with Pt, O_2(air)|ZrO_2 serving as the reference electrode. The electrochemical behavior of Ni^{2+} on an Ir electrode was investigated in SiO_2-CaO-MgO-Al_2O_3 molten slag at 1673 K using techniques including cyclic voltammetry (CV), square wave voltammetry (SWV), chronopotentiometry (CP), and potentiostatic electrolysis. The results demonstrate that both diffusion of O^{2-} in the molten slag and electromigration of O^{2-} within the ZrO_2 solid electrolyte are not rate-determining steps for the reduction of electroactive ions. It is feasible to study the electrochemical behavior of Ni^{2+} in molten slag using this controlled oxygen flow electrolytic cell under the present experimental conditions.

The reduction of Ni^{2+} on the Ir electrode in molten slag is found to be a reversible, single-step reaction controlled by diffusion. Two diffusion coefficients of Ni^{2+} in molten slag containing 3% NiO, derived from CV and CP respectively, are (3.50$±0.18)×10^{-6}$ and (2.80$±0.22)×10^{-6}$ cm^2/s, which are consistent with values reported in relevant literature.

KEY WORDS Ni^{2+}, molten slag, electrochemical behavior, cathodic process, electrolytic cell with controlled oxygen flow

Introduction

The iron and steel metallurgy industry represents one of the major sources of greenhouse gas CO_2 emissions [?, ?]. Using inert electrodes to electrolytically reduce molten oxide containing iron oxides to produce metallic Fe is a potential short-process steelmaking technology that could significantly reduce or even eliminate CO_2 emissions while saving energy and protecting the environment

[?, ?]. Ni is an important alloying element in steel that enhances corrosion resistance. During electrolysis of slag containing Ni and Fe oxides, codeposition of Ni and Fe can be used to further smelt Ni-containing steels (including stainless steel). To determine reasonable process parameters for Ni extraction via electrolysis, it is essential to understand the electrochemical behavior of nickel oxides in high-temperature molten slag.

Semkow et al. [?] studied the electrochemical behavior of Ni^{2+} in CaO-MgO-SiO_2 slag using cyclic voltammetry under air atmosphere, concluding that Ni^{2+} reduction on Pt electrodes is reversible and obtaining the diffusion coefficient of Ni^{2+} in molten slag. Colson et al. [?] demonstrated that under CO_2 atmosphere, NiO reduction in SiO_2-Al_2O_3-MgO-CaO slag produced Ni that primarily dissolved into the Pt electrode rather than the slag, with the diffusion coefficient of Ni in Pt being three orders of magnitude smaller than that of Ni^{2+} in slag. Strycker et al. [?] employed multiple electrochemical methods to show that Ni^{2+} reduction to Ni in glass melts is a reversible process controlled by Ni^{2+} diffusion. Other researchers [?] have also measured diffusion coefficients of Ni^{2+} in glass melts using electrochemical techniques.

However, most existing studies on Ni^{2+} electrochemistry [?, ?, ?] used Pt as the reference electrode, which is not conducive to theoretical analysis of NiO electrolysis in slag. Other studies [?, ?] were conducted primarily in glass melts below 1473 K, and the high viscosity of glass melts makes them unsuitable as media for Ni extraction via electrolysis. Furthermore, investigations of electrochemical behavior in molten slag are often limited by electrode stability (particularly reference electrodes), electrolytic cell container stability, electronic conductivity of slag, and interference from impurity ions, making high-temperature electrochemical experiments challenging.

ZrO_2-based solid electrolytes exhibit high oxygen ionic conductivity and low electronic conductivity at high temperatures, along with strong corrosion resistance. Solid electrolyte cells constructed from these materials have found extensive applications in metallurgical industry and scientific research [?], including measurements of oxygen activity [?, ?] and diffusion coefficients [?, ?] in metal melts, FeO activity in molten slag [?, ?], electrolytic refining of metal melts [?, ?], and metal extraction from molten salts or slags containing dissolved oxides [?]. Additionally, many studies [?, ?, ?] have employed Pt, O_2(air)|ZrO_2 as reference electrodes for three-electrode electrochemical measurements.

Based on the concept of controlled oxygen flow metallurgy [?], this work constructed a novel controlled oxygen flow electrolytic cell integrated with a Pt, O_2(air)|ZrO_2 reference electrode structure, using an MSZ tube as both the working electrode/auxiliary electrode compartment separator and the electrolytic cell container. Using cyclic voltammetry, square wave voltammetry, potentiostatic electrolysis, and chronopotentiometry, we investigated the electrochemical behavior of Ni^{2+} on Ir electrodes in SiO_2-CaO-MgO-Al_2O_3 molten slag at 1673 K, aiming to provide theoretical foundations for metal extraction via molten slag electrolysis.

1. Experimental

1.1 Preparation of Pre-Melted Slag All reagents used were analytically pure. SiO_2, $CaCO_3$, MgO, and Al_2O_3 powders were separately heat-treated in a box-type resistance furnace at 1223 K for 6 h to thoroughly remove moisture and carbonates. These powders were then mixed in the proportion 47%SiO_2-28%CaO-16%MgO-9%Al_2O_3 (by mass) to serve as the base slag. This base slag had a basicity (mass ratio of CaO to SiO_2) of 0.6, a melting point below 1573 K, and exhibited low viscosity with high conductivity [?]. The low basicity was chosen to minimize potential corrosion of ZrO_2 by the slag. Green NiO was added to the base slag at specific proportions. The mixed slag material was placed in a high-purity corundum crucible, which was then positioned in a $MoSi_2$-heated alumina tube furnace. The furnace was purged with Ar gas that had been purified through secondary deoxygenation using Cu wire and Mg chips at 853 K and dried with silica gel. The furnace was heated to 1773 K and held for 1 h to melt the slag. The crucible containing the molten slag was then rapidly removed and quenched in water. The solidified pre-melted slag was crushed and stored in a desiccator for later use.

1.2 Construction of the Electrolytic Cell The electrolytic cell consisted of a one-end-closed MSZ tube (inner diameter 7.3 mm, outer diameter 10 mm, length 79 mm) and three electrodes, with the structural schematic shown in [Figure 1: see original paper]. Two adjacent areas on the outer surface of the closed end of the MSZ tube were coated uniformly with Pt paste using a homemade feather brush. After drying, the coated tube was sintered in an open box-type resistance furnace at 1173 K for 30 min. After natural cooling, the Pt paste coating and sintering process was repeated once more to obtain a porous Pt electrode with strong adhesion and good conductivity (resistance below 0.2 Ω between any two points). The porous Pt electrode near the bottom served as the auxiliary electrode (area = 1.570 cm^2), while the other served as the reference electrode (area = 1.256 cm^2). Both auxiliary and reference electrode leads were Pt wires (diameter 0.5 mm). Molten slag was contained within the MSZ tube, with approximately 0.8 g of pre-melted slag used for each experiment. An Ir wire (purity 99.95%, diameter 0.5 mm, length 30 mm) served as the working electrode, with one end immersed in the molten slag and the other end connected to a Pt wire lead. All electrode leads were protected by fine alumina tubes.

1.3 Experimental Methods Based on literature [?, ?], the electrolytic cell was designed as a three-electrode system, as shown in [Figure 1: see original paper]. Electrochemical measurements were controlled and recorded using a CHI1140A electrochemical analyzer. The electrolytic cell was placed in the constant temperature zone of a $MoSi_2$-heated high-temperature tube furnace. Purified, dried Ar gas was introduced into both the furnace chamber (400 mL/min) and the MSZ tube (20 mL/min) as protective atmosphere. The furnace heating rate was set at 5 K/min, with temperature measured by a Type B thermocouple. After the furnace reached 1673 K, it was held for 30 min. During this holding period, the working electrode was slowly inserted into the molten slag (without contacting the inner wall of the MSZ tube). The slag surface level was determined by observing abrupt changes in the open-circuit potential-time curve (shown in [Figure 2: see original paper]). Preliminary experiments indicated that electrode depth around 5 mm had minimal influence on the measured curves; therefore, the working electrode insertion depth was maintained at 5 mm for all experiments (working electrode area A = 7.85×10^{-2} cm^2). Finally, the furnace atmosphere was switched from Ar to dry air (flow rate 400 mL/min) to establish a stable oxygen partial pressure at the Pt, O_2(air)|ZrO_2 reference electrode outside the MSZ tube. During switching, the open-circuit potential responded rapidly and eventually stabilized at approximately -0.05 V. After the open-circuit potential-time curve stabilized under air atmosphere, pre-scanning was performed until the electrode condition became stable. Formal experiments commenced after completion of pre-scanning.

Electrochemical measurements were conducted primarily using cyclic voltammetry, square wave voltammetry, and chronopotentiometry. The first two techniques employed the instrument' s built-in positive feedback function for 100% IR drop compensation (without causing curve oscillation or distortion). Only chronopotentiometry could not be IR-compensated due to instrument limitations. All potentials reported herein are relative to the Pt, O_2(air)|ZrO_2 reference electrode. For consecutive electrochemical tests on the same slag sample, the open-circuit potential-time curve was measured before each test until a relatively stable quasi-steady state was achieved.

Additionally, slag containing 3% NiO was electrolyzed potentiostatically at -0.25 V, -0.70 V, and -1.30 V for 100, 100, and 30 min, respectively. The electrolyzed samples were examined using a Nova 400 Nano scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) analysis.

2. Results and Discussion

2.1 Determination of Scanning Potential Range for Cyclic Voltammetry Nickel exists in two oxidation states: Ni^{2+} and Ni^{3+}. However, in silicate molten slag, Ni typically exists stably as Ni^{2+} even under air atmosphere or when Ni_2O_3 is added [**?**, **?**]. The NiO reagent used in this work was confirmed by X-ray diffraction (XRD) analysis to be pure NiO. Therefore, it can be determined that under the Ar-protected conditions of this experiment, Ni exists as Ni^{2+} rather than Ni^{3+} in the silicate molten slag.

[Figure 3: see original paper] shows cyclic voltammetric curves for slags with different NiO concentrations. Analysis of the curve for slag without NiO (blank slag) reveals that during the negative scan, the current remains stable and near zero within the range of 0 to -1.2 V, indicating good electrochemical stability without chemical reactions and negligible impurity interference. When the potential reaches -1.2 V, the current (negative direction) increases sharply, forming reduction peak C1. Using FactSage thermodynamic software [?] to calculate the activities of slag components, and assuming an oxygen partial pressure of 21 kPa in air and unit activity of metal products (closest to experimental conditions), the theoretical decomposition voltage of SiO_2 in slag without NiO is the most positive (approximately -1.6 V). Therefore, reduction peak C1 should correspond to premature Si deposition, which occurs due to depolarization from formation of low-melting-point alloys between deposited Si and the Ir electrode [?]. During the positive scan, a corresponding Si oxidation peak A1 appears, with the current finally stabilizing at zero and returning to the starting point. Peak A1 actually contains two oxidation peaks corresponding to oxidation of pure Si and Si dissolved in the Ir electrode. To avoid Si deposition, the scanning potential range for NiO-containing slag was selected as 0 to -0.8 V, which corresponds to the curve ranges for wNiO = 1%, 3%, and 5% in [Figure 3: see original paper].

Taking the curve for wNiO = 3% in [Figure 3: see original paper] as an example for analysis: Similar to the NiO-free curve, the wNiO = 3% curve shows a charging current segment before metal deposition, followed by a sharp current increase indicating the onset of metal deposition. FactSage thermodynamic software calculated the theoretical decomposition voltage of NiO under conditions closest to this experiment as -0.56 V. By drawing tangents, the actual decomposition voltage of the reduced metal oxide was determined to be approximately -0.42 V, suggesting that the deposited metal is Ni. The deposited Ni forms an alloy with the Ir working electrode, causing the actual decomposition voltage of NiO to be more positive than the theoretical value. Therefore, peaks A2/C2 correspond to the Ni oxidation/reduction peaks. However, for curves with wNiO = 1%, 3%, and 5%, the scan end point does not coincide with the starting point, unlike the wNiO = 0 curve. Fujishima et al. [?] attributed this phenomenon to different concentration distributions of electroactive species on the electrode surface at the two moments, indicating that Ni^{2+} diffusion in this slag system is relatively slow.

2.2 Square Wave Voltammetry Square wave voltammetric curves for slag with wNiO = 3% were measured in the frequency range of 20-40 Hz and compared with the curve for NiO-free slag (blank) at 30 Hz, as shown in [Figure 4: see original paper]. The curve for NiO-containing slag exhibits only one reduction peak at approximately -0.52 V, consistent with the potential of the Ni^{2+} reduction peak C2 in [Figure 3: see original paper], indicating that Ni^{2+} reduction occurs in a single step to Ni. Examination of the square wave voltammetric curves at different frequencies in [Figure 4: see original paper] shows that the peak potential remains essentially unchanged with frequency, providing preliminary evidence that Ni^{2+} reduction is a reversible reaction.

2.3 Potentiostatic Electrolysis [Figure 5: see original paper] shows SEM images of Ir electrode cross-sections after potentiostatic electrolysis of slag containing 3% NiO at different potentials. At -0.25 V, the Ir electrode cross-section shows no significant change. When the potential was increased negatively to -0.70 V and -1.30 V, obvious layering appears in the electrode cross-section. EDS analysis of the Ir electrode cross-sections ([Figure 6: see original paper]) indicates that at -0.25 V, no new substance deposits on the electrode surface; at -0.70 V, the layered region consists of Ir-Ni alloy, demonstrating Ni deposition; at -1.30 V, the layered region consists of Ir-Ni-Si alloy, indicating deposition of both Ni and Si. This corresponds to the reduction peaks observed in the cyclic voltammetric curves in [Figure 3: see original paper]. The layering on the Ir wire results from alloy formation among Ir, Ni, and Si. Therefore, peaks C1 and C2 can be confirmed as the reduction peaks of Si^{4+} and Ni, respectively.

Using FactSage thermodynamic software and following the calculation method in reference [?], the equilibrium mass fractions of slag and solid phases were calculated for the SiO_2-CaO-MgO-Al_2O_3-NiO slag and MSZ composition conditions in this experiment. The results show that the solubility of ZrO_2 in molten slag is extremely low, only about 0.9%. [Figure 7: see original paper] shows SEM images of the MSZ tube-slag interface after potentiostatic electrolysis of slag containing 3% NiO. At -0.70 V, even after 100 min of electrolysis, the MSZ tube at the interface remains dense and intact, indicating minimal slag corrosion of the MSZ tube. At -1.30 V, however, some ZrO_2 grains at the interface show detachment, indicating that high negative potentials intensify slag penetration and corrosion of the MSZ tube, leading to ZrO_2 grain detachment. No new phases were detected at the interface, which is particularly important for maintaining the directional migration channel of oxygen ions during electrochemical testing. This work primarily employed electrochemical transient testing techniques with very short polarization times, continuously changing polarization directions, and mostly maintained polarization potentials within the relatively low range of -0.8 to 0 V. Therefore, dissolution of the MSZ tube in molten slag can be neglected, and the properties of both the MSZ tube and molten slag can remain relatively stable.

2.4 Analysis of Ni^{2+} Electrochemical Reduction Behavior [Figure 8: see original paper] shows the effect of initial scan cycles on cyclic voltammetric curves with a fresh Ir electrode. As the number of cycles increases, the peak potential shifts in the negative direction and the peak current increases slightly. However, this effect diminishes with increasing cycles; the difference between the 1st and 2nd cycles is obvious, while curves for the 4th and 5th cycles almost overlap. This occurs because the electrode surface condition is unstable when a fresh electrode is first immersed in the slag. Guan et al. [?] attributed this to a roughening effect that increases the effective surface area. After about 4 cycles, the electrode surface condition stabilizes, the peak current no longer increases, and the curves become stable. Considering the instability caused by fresh electrodes, all curves presented in this work were obtained after stabilization through pre-scanning.

[Figure 9: see original paper] shows cyclic voltammetric curves for slag containing 3% NiO at different scan rates (v). During the negative scan from the starting point, Ni^{2+} in the molten slag diffuses toward the Ir cathode, while O^{2-} in the slag diffuses to the slag/MSZ tube interface and migrates through the MSZ tube to reach the MSZ tube/Pt anode interface. When the scanning potential reaches the reduction potential of Ni^{2+}, Ni^{2+} reduces on the Ir cathode, producing a reduction peak C2 corresponding to the electrode reaction: Ni^{2+} + 2e$^-$ → Ni. Reduction peak C2 is broad and not sharp, characteristic of a diffusion-controlled peak where the product is soluble [?], indicating that the deposited Ni forms an Ir-Ni alloy with the Ir substrate [?]. This corresponds to the potentiostatic electrolysis results ([Figure 5b: see original paper]) and is consistent with findings by Colson et al. [?]. Simultaneously with Ni^{2+} reduction at the Ir cathode, O^{2-} migrating through the MSZ tube is oxidized at the porous Pt anode outside the tube: 2O^{2-} → O$_2$ + 4e$^-$, with O$_2$ entering the air. During the reverse scan, Ni on the Ir anode oxidizes, producing a broad nickel alloy oxidation peak, and the resulting Ni^{2+} diffuses into the bulk slag. Meanwhile, O$_2$ in the air is reduced to O^{2-} at the porous Pt cathode outside the MSZ tube: O$_2$ + 4e$^-$ → 2O^{2-}, which then migrates through the MSZ tube into the slag and diffuses to the Ir anode surface until the scan ends at 0 V.

[Figure 10: see original paper] shows reversal chronopotentiometry curves. The transition time t was determined by the tangent method, yielding a ratio of reduction/oxidation transition times t$_1$/t$_2$ 2.74 for Ni^{2+}/Ni, further confirming the solubility of the product [?]. The plateau corresponding to t$_3$ should be attributed to oxidation of the Ir electrode.

A plot of cathodic peak current I c versus v^1/^{2} from [Figure 9: see original paper] is shown in [Figure 11: see original paper]. Linear fitting reveals a good linear relationship passing near the origin. Additionally, peak positions in [Figure 9: see original paper] shift only slightly with scan rate, a change that can be neglected. Therefore, Ni^{2+} reduction is inferred to be a diffusion-controlled reversible reaction. For a reversible soluble reaction system, I c follows the Randle-Sevcik equation [?, ?]:

$$I_{pc} = -0.4463\, n^{3/2} F^{3/2} (RT)^{-1/2} A D^{1/2} C_0 v^{1/2}$$

where n is the number of electrons transferred (n = 2), F is the Faraday constant (F = 96500 C/mol), R is the molar gas constant (R = 8.314 J/(mol · K)), T is the thermodynamic temperature (T = 1673 K), A is the working electrode area (A = 0.0785 cm^2), C$_0$ is the bulk concentration of the electroactive species Ni^{2+}, and D is the diffusion coefficient of Ni^{2+} (cm^2/s).

The density of slag with approximate composition 44.8%SiO$_2$-31.3%CaO-8.9%MgO-15%Al$_2$O$_3$ at 1673 K was obtained from literature [?] as 2.64 g/cm^3, from which the Ni^{2+} molar concentration was calculated as C$_0$ = 1.06$×10^{-3}$ mol/cm^3. From the slope of the fitted line in [Figure 11: see original paper], $D^{1/2} = -0.0499 \pm 0.00132$ was obtained, yielding D = (3.50$±0.18)×10^{-6}$

cm^2/s. compiles diffusion coefficients of Ni^{2+} in similar slag systems from literature [**?**, **?**, **?**, **?**], showing that the results are comparable.

[Figure 12: see original paper] shows chronopotentiometric curves for slag containing 3% NiO at different cathodic currents. At t = 0, the potential jumps to the reduction potential (approximately -0.5 V), followed by a Ni^{2+} reduction plateau A. At approximately -0.69 V, the potential begins transitioning to the Si^{4+} reduction plateau B. Compared with the reduction potential from cyclic voltammetry (actual decomposition voltage of -0.42 V), the chronopotentiometric curves show more negative potentials, likely because cyclic voltammetry included IR drop compensation while chronopotentiometry did not. However, both values are close to the theoretical decomposition voltage of -0.56 V.

[Figure 13: see original paper] shows the I versus It^1/^{2} plot corresponding to [Figure 12: see original paper]. The It^1/^{2} value remains nearly constant with changing cathodic current I, indicating that Ni^{2+} reduction is diffusion-controlled [**?**]. Meanwhile, the linear relationship between E and ln[(t^1/^{2} - t^1/^{2})/t^1/^{2}] in [Figure 14: see original paper] demonstrates the reversible characteristics of the chronopotentiometric curves in [Figure 12: see original paper] [**?**]. Therefore, the Ni^{2+} reduction plateau A follows the Sand equation [**?**]:

$$It^{1/2} = \frac{1}{2} nFAD^{1/2} C_0 \pi^{1/2}$$

where I is the cathodic current (A) and t is the transition time (s). Using equation (2), D = (2.80$±0.22)×10^{-6}$ cm^2/s was calculated, which is close to the value obtained from cyclic voltammetry in this work.

2.5 Cathodic Process of Ni^{2+} on Ir Electrode in Molten Slag After NiO addition to the slag, it can be considered to exist as Ni^{2+} and O^{2-}. The molten slag, serving as a supporting electrolyte, can be regarded as an ionic conductor primarily conducting via cations such as Ca^{2+} and Mg^{2+} [**?**]. Therefore, the transport number of O^{2-} in molten slag is small, and O^{2-} moves primarily by diffusion under applied potential. At high temperatures, O^{2-} has a high ionic transport number in the MSZ tube and moves primarily by electromigration. Under the present experimental conditions, the current through the controlled oxygen flow electrolytic cell can be considered to be primarily pure O^{2-} ionic current (with a small amount of non-Faradaic charging current). When electrochemical reactions occur in the molten slag, the diffusion rate of O^{2-} in the slag and the electromigration rate of O^{2-} in the MSZ tube remain equal at all times, provided the slag maintains electrical neutrality and no oxygen accumulates in the cell.

During negative potential scanning, electroactive species in the molten slag (such as ions and elements of Ni or Si) can be reduced or oxidized at the working electrode. The oxygen ion current in the MSZ tube does not always increase with applied potential but changes with the redox reactions of electroactive species. Similarly, square wave voltammetry ([Figure 4: see original paper]) and chronopotentiometry ([Figure 10: see original paper] and [Figure 12: see original paper]) can reflect different electrochemical characteristic information of electroactive species (such as Ni^{2+}) at the working electrode. It can be concluded that O^{2-} diffusion in molten slag and electromigration in the MSZ tube do not become limiting steps for reduction of electroactive species (such as Ni^{2+}) at the Ir working electrode. Furthermore, the controlled oxygen flow electrolytic cell can reduce or eliminate interference from electronic conductivity of slag and non-oxygen ions. The Pt, O_2(air)|ZrO_2 reference electrode responds quickly with good reversibility at high temperatures [**?**], producing stable and smooth electrochemical curves convenient for mathematical treatment. The results of this work also indicate that slag corrosion of the MSZ tube actually has minimal impact on electrochemical test results. Therefore, using ZrO_2-based solid electrolyte tubes to construct a novel controlled oxygen flow electrolytic cell with Pt, O_2(air)|ZrO_2 as the reference electrode is feasible for studying the electrochemical behavior of nickel ions in molten slag.

The cathodic process of electroactive Ni^{2+} on Ir electrodes in SiO_2-CaO-MgO-Al_2O_3 molten slag at 1673 K can be analyzed as follows: (1) Ni^{2+} in molten slag diffuses to the Ir electrode surface; (2) Ni^{2+} gains electrons at the Ir electrode surface, reduces, and forms an alloy with the Ir electrode: $Ni^{2+} + 2e^- \rightarrow Ni$ (Ir-Ni alloy). Based on this analysis, Ni^{2+} reduction in molten slag is a single-step, diffusion-controlled reversible process, consistent with conclusions by Semkow et al. [**?**] and Strycker et al. [**?**].

Conclusions

1. A novel controlled oxygen flow electrolytic cell was constructed by integrating an MSZ solid electrolyte tube with a Pt, O_2(air)|ZrO_2 reference electrode. O^{2-} diffusion in molten slag and electromigration in the MSZ tube do not become limiting steps for reduction of electroactive ions, making it feasible to study the electrode process of Ni^{2+} in molten slag using this cell.

2. In SiO_2-CaO-MgO-Al_2O_3 molten slag, Ni^{2+} undergoes a single-step reversible reduction process controlled by diffusion. Ni^{2+} first diffuses to the Ir electrode surface, then reduces and forms an alloy with the Ir electrode. Diffusion coefficients D of Ni^{2+} in molten slag containing 3% NiO at 1673 K, calculated using cyclic voltammetry and chronopotentiometry, are (3.50$±0.18)×10^{-6}$ and (2.80$±0.22)×10^{-6}$ cm^2/s, respectively. The values obtained by the two electrochemical techniques are similar and agree well with literature values.

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Note: Figure translations are in progress. See original paper for figures.

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