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Calciothermic reduction of NiO by molten salt electrolysis of CaO in $CaCl_2$ melt

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ABSTRACT

Metallic nickel powders with low and uniform residual oxygen content were produced from NiO using the molten salt electrolysis of CaO in $CaCl_2$ melt. Suitable amount of CaO for the reduction was in the range of 0.5–3.0 mol% CaO.

The electrical isolation of NiO from both electrodes could produce metallic Ni in $CaCl_2$ melt. Separating the metal oxides from the cathode confirmed the mechanism of calciothermic reduction that the electrolysis of dissolved CaO in $CaCl_2$ melt produces Ca, and that the dissolved Ca in molten $CaCl_2$ successfully reduces NiO to metallic Ni. An average of about 600 ppm oxygen in Ni sample was achieved directly from oxide, when NiO was detached from the cathode.

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1. Introduction

A direct way of oxide reduction by using molten salt electrolysis has been intensely investigated for the past decade. Metal oxides are immersed into a bath of molten salt and electrolyzed by applying electric field. The metallic products are formed at the cathode and the carbonic gases are expelled at the anode [1–13]. Aside from pure metal production, this process was tried in producing some alloys and intermetallic compounds directly from the oxide mixture [14–19], making it an attractive reduction method. Varieties of salts are employed as the electrolytes, but the salt most largely used is $CaCl_2$-based salt because calcium chloride can dissolve up to 20 mol% CaO [20–22] and because a small addition of CaO in $CaCl_2$ was found to improve the rate of reduction and deoxidation [3–9,12,13].

Two notable yet conflicting ideas on the effect of calcium oxide addition to the molten salt were presented by the OS process and FFC-Cambridge process.

Calcium chloride can dissolve 2–4 mol% Ca at 1173 K in equilibrium [23–28]. OS process speculated that the presence of Ca dissolved in molten salt was responsible for reduction [1–9]. The dissolved Ca reacts with titanium dioxide producing metallic titanium and CaO as presented in Eq. (1) [1–3]. When an electric field is applied between the two electrodes, the electrolysis of CaO occurs to produce Ca near the cathode and at the same time two carbonic gases are produced at the anode as shown by Eqs. (3) and (4), respectively. CaO becomes the source of Ca for the calciothermic reduction of metal oxide in molten $CaCl_2$ and for the further deoxidation (Eqs. (1) and (5)), producing a highly reduced metal with low residual oxygen.

$$TiO_2 + 2Ca = Ti + 2\underline{CaO}(\text{reduction}) \tag{1}$$

$$\underline{CaO} = Ca^{2+} + O^{2-} \tag{2}$$

$$Ca^{2+} + 2e^- = \underline{Ca}(\text{at cathode}) \tag{3}$$

$$nO^{2-} + C = CO_n + 2ne^-(n = 1\text{or}2)(\text{at anode}) \tag{4}$$

$$\underline{O}(\text{inTi}) + Ca = \underline{CaO}(\text{deoxidation}) \tag{5}$$

FFC-Cambridge process [10–19], on the other hand, is considered as the concept of cathodic oxygen ionization of the solid oxide in the molten salt to reduce the pelletized metal oxide precursor which is served as the cathode (Eq. (6)). FFC-Cambridge cathodic reaction is presented by the following equations [10]:

$$TiO_2 + 4e^- = Ti + 2O^{2-}(\text{inCaCl}_2)(\text{electro-reduction}) \tag{6}$$

$$\underline{O}(\text{inTi}) + 2e^- = O^{2-}(\text{inCaCl}_2)(\text{electro-deoxidation}) \tag{7}$$

It was asserted that a moderate concentration of CaO promotes the better reaction rate due to the enhanced oxide ion transfer across the electrolyte [12,13]. CaO content in the electrolyte is a key parameter to the process. FFC mechanism argued that the presence of dissolved Ca in the electrolyte causes an undesired side effect because it imparts a degree of electronic conduction on the electrolyte and lowers current efficiency [11,13]. Therefore, Ca is not a requirement for reduction in FFC mechanism.

The proper CaO concentration suitable for reduction has been rarely investigated, despite the fact that calcium oxide addition

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to molten calcium chloride yields positive results. Namely, in the purely calciothermic reduction of TiO_2 without external electrochemical potential [3], 0.5 mol% CaO in the $CaCl_2$ melt resulted to the better deoxidation, i.e., the lowest residual oxygen in the reduced metallic titanium was achieved. Therefore, it has often taken as the standard condition in CaO concentration [4–9]; however, no experimental optimizations have been given in the concept of OS process. This work aims to examine the CaO concentration that is favourable for reduction and deoxidation of metal oxide in the case of electrolysis in the molten $CaCl_2$ bath.

This work will also characterize OS process from FFC-Cambridge process to prove the calciothermic reduction and deoxidation by electric isolation of the metal oxide from the cathode during electrolysis. In TiO_2 reduction, the complex oxides such as $CaTiO_3$ and Ca_2TiO_4 were often formed as the intermediate phases during reduction to pure metallic titanium [3–13], and these formations disturbed the detailed analysis on the CaO concentration suitable for reduction. Nickel oxide was used in this work because it was found in the preliminary experiments [9] that nickel oxide did not lead to the formation of any complex oxides, alloys or intermetallic compounds with calcium when NiO was reduced in molten $CaCl_2$. In their paper, Yan and Fray, also produced metallic nickel directly from the oxide with no other lower oxides or Ca–Ni alloys by-product. Detailed analysis on NiO reduction using molten salt electrolysis, however, has not been reported.

When NiO is in physical contact with C, solid state carbothermic reduction may occur at 1173 K ($\Delta G^{\circ} = -128.9\,\mathrm{kJ\,mol^{-1}}$[29]). However, it was reported that the carbothermic reduction was very slow at 1173 K; for instance only 30% reduction after 6 h [30]. This work excludes any possibility of carbothermic reduction; there was no physical contact between the oxides and carbon in molten $CaCl_2$.

When NiO was mixed with another oxide such as TiO_2, CeO_2 or MgO, it was reported that NiO was preferentially reduced to nickel metal before the reduction of Ti, Ce or Mg oxide, respectively, in the $CaCl_2$ melt [15–19]. This indicates that the thermodynamic stability of NiO is not as strong as compared with the other oxides. It is proved thermodynamically that the oxygen potential of NiO is higher than those of the other oxides. Thus, NiO was a suitable oxide to study the initial stage of reduction in the molten $CaCl_2$.

2. Experimental

Six hundred grams of anhydrous $CaCl_2$ (>95%, Wako Chemical Co.) was mixed with CaO (99.9%, Kanto Chemical) calcined in air, and used as electrolyte by filling inside a magnesia crucible (Fig. 1). A basket-like cathode was prepared by wrapping two nickel disks (15 mm in diameter, a few mm thick) doubly in Ni net (150 mesh). 1.5 g of nickel monoxide (>99%, Wako Chemical Co.) was loosely poured inside the cylindrical basket. The basket was connected to a stainless steel rod as shown in Fig. 1. A graphite electrode (10 mm in diameter) was used as the anode. The electrodes were attached to the cover of stainless steel vessel using silicone stopper, and a distance of about 20 mm between the anode and cathode was maintained throughout all the experiments.

The magnesia crucible was heated slowly in vacuum to 873 K. This condition was maintained at this temperature for at least 36 ks to ensure that any hydrates will be completely decomposed and the moisture in the vessel removed. After moisture removal, argon gas was charged into the vessel. The temperature was gradually raised to 1173 K for 10.8 ks in Ar gas environment and allowed to stabilize for 1.8 ks. The electrodes were submerged into the salt bath at the depth of about 10 mm above the bottom of the crucible. A constant voltage of 3.1 V was then applied to the electrodes. Current between the two electrodes were recorded every 5 s. After 1.8 ks, power supply was terminated and the electrodes were pulled up to the upper part of the vessel. The furnace was then cooled-down to room temperature.

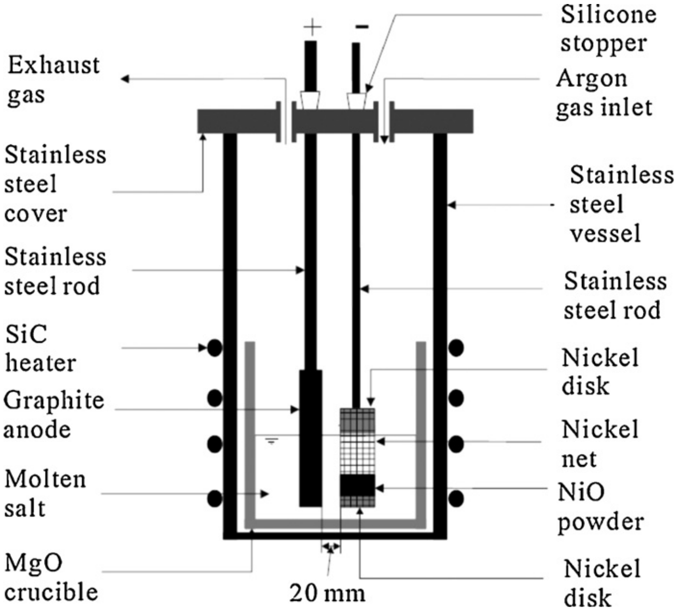

Fig. 1. Experimental apparatus for electrolysis.

The basket-like cathode was taken out of the furnace, washed with distilled water and then placed in an ultrasonic vibration cleaner. The slightly sintered sample was taken out of the Ni basket and carefully sliced into 3 parts with approximately 2.5 mm circumferential interval from the Ni net where the sample attached. These 3 parts were then separately crushed into fine grains. In order to remove the solidified salt residue from the specimens completely, the samples were again washed by distilled water, acetic acid, distilled water, ethanol and acetone in exact order. The specimens were then dried in vacuum. Phases were examined using X-ray diffraction (XRD) analysis. Residual oxygen content was determined by the inert gas fusion-infrared adsorption method using LECO TC600 oxygen/nitrogen analyzer. Morphologies of the resulting powders were observed under the scanning electron microscope (SEM).

3. Results and discussion

3.1. Concentration dependency of the current

A constant voltage of 3.1 V between two electrodes was applied in all the electrolysis. Except for CaO concentration, all the other experimental conditions were the same for all the runs. For example, the quantity of NiO, the distance between the two electrodes, electrolysis time, holding temperature and applied voltage were set as the same for all experiments.

In OS mechanism, the theoretical charge, Q_o, is defined as the charge required to generate stoichiometric amount of Ca reductant for the reduction of the filled amount of NiO. On the other hand, Q_o, is also defined as the theoretical charge for oxygen ion removal from the served oxide pellet in case of FFC mechanism. Thus the defined Q_o are identical. The supplied charge, Q, was calculated by integrating current with respect to time. Consequently, the ratio of Q/Q_o is used as normalized parameter for the amount of supplied electric charge.

Table 1 listed the calculated Q/Q_o at various CaO concentrations electrolyzed for 1.8 ks at 1173 K. After 1.8 ks electrolysis, the

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