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Verification of the electro-decomposition of the CaO component in equimolar $CaCl_2$-NaCl molten salt during the direct electrolysis of ilmenite in a two-terminal chamber

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ABSTRACT

In the present research, the decomposition of CaO was verified by observing the calciothermic reduction of ilmenite powders that were placed near the negative terminal without a direct connection. With the addition of 0–2 mol% CaO in equimolar $CaCl_2$-NaCl molten salt, it was demonstrated that CaO was electrochemically decomposed to calcium metal, and the metallic phase acted as the reductant to further reduce the ilmenite with the formation of intermediates Fe, $CaTiO_3$, Fe_2Ti and FeTi. A sustainable reduction of $CaTiO_3$ commenced with greater calcium metal participation, and the calcium metal content was determined using the CaO concentration in the molten salt. The effect of CaO concentration on the direct electrochemical reduction of a bulk ilmenite pellet was studied. The results proved that the dissolved CaO had an appreciable effect on the phase transformation. Upon the addition of 1 mol% CaO into equimolar $CaCl_2$-NaCl molten salt, the deoxidization rate of ilmenite was promoted, leading to the complete production of an FeTi alloy in fine and homogeneous microstructures with a particle size of 2–8 μm. A lower CaO content (0–0.5 mol%) set the oxide ion transfer limit, and a higher content (more than 1.5 mol%) raised the electronic background current, resulting in charge loss and insufficient electricity for the electrochemical reduction of ilmenite.

1. Introduction

Recently, the direct extraction of metals and alloys in solid state from their complex multicomponent oxide powders with anisotropic particle morphologies through the use of molten salt electrolysis has attracted considerable attention [1,2]. Oxygen removal from solid oxides is the essence of this technique. Thus, two promising approaches containing metallothermic and electrochemical deoxidization routes such as the Fray-Farthing-Chen Cambridge process (FFC) [3], the electrolysis-assisted calciothermic reduction process (OS) [4], the Electronically Mediated Reaction process (EMR) [5], the Preform Reduction process (PRP) [6] and the Solid Oxide-Oxygen-Ion Conducting Membrane process (SOM) [7] are introduced for the direct reduction of oxides.

Among these popular methods, the FFC and OS techniques have been successfully applied to the production of many metals and alloys, e.g., Nb [8], Ti [9,10], Ge [11], Si [12], NiTi [13], FeTi [14–17], and Ti_5Si_3 [18]. The FFC process focuses on the extraction of metals by electrolysing oxides in molten salt using graphite as the consumable anode and the sintered porous oxide pellet connected to the inert electrode as the cathode. Under appropriate cell voltages, oxygen in the cathodic solid oxides is continuously ionized, dissolved in electrolyte, and discharged to generate gaseous carbon-oxides at the graphite anode [19]. This method has been applied to convert metallic oxides into metals and alloys with the advantage of crystal growth at temperatures far below the melting point of the synthetic product phase. The as-produced metals also retain the shape of the mineral precursor with some decrease in the

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dimensions. Thus, it is possible to control the process conditions to produce either powdery, porous or dense metal products to satisfy the industrial demand. This method has been applied on a pilot scale at the Metalysis company (https://www.metalysis.com) in England.

Another metallurgical extraction process is the calciothermic reduction process, known as the OS process [20]. The essence of this method is the utilization of calcium metal as the reductant for metal production. Metallic calcium can be easily obtained via the direct electro-decomposition of CaO dissolved in the electrolyte or by the cathodic potentiostatic electro-deposition of Ca^{2+} from the electrolyte. The characteristics of this method can be summarized with the example of calciothermic reduction of TiO_2 as follows: (1) calcium metal is used as a reductant to directly reduce titanium dioxide powder to elemental titanium; (2) the byproduct CaO is then re-electrolysed to metallic Ca in the fused $CaCl_2$-based salts; and (3) all reactions can be operated in single molten salt.

The deoxidization mechanisms have been debated with a particular focus on the type of reduction during the electrolysis process in the $CaCl_2$-based molten salt chamber. For instance, in the FFC process, the reduction of oxide relies on the direct e^- uptake from the current collector. Along with constant electrolysis, the byproduct O^{2-} dissolves into molten salt and increases the oxygen potential of the electrolyte. The O^{2-} concentration, which is generally equivalent to the dissolved CaO content, should be decomposed theoretically because the injected cell voltages (2.8–3.2 V) are beyond the CaO decomposition voltage (lower than 2.4 V at 900 °C). As a result, calcium metal is probably deposited at the inert cathode and should dissolve into equimolar $CaCl_2$-NaCl molten salt with a solubility of merely 1.86 mol% while the solubility of CaO in equimolar $CaCl_2$-NaCl melt is 7 mol% [20–22]. In such a case, the oxide precursor can also be calciothermically reduced with the aid of calcium metal. However, it appears that it is difficult to provide unambiguous evidence for the formation of calcium metal. In addition, it can be expected that the electrochemical production of calcium metal will consume electricity, inducing charge competition between the decomposition of CaO and the direct electrolysis of cathodic oxides. Systematic studies are still required to reveal the decomposition behaviour of CaO. Efforts have been made to determine the peculiar role that CaO plays in molten salt. Wang et al. [22] have studied the electrochemical behaviour of CaO in a 0.5% CaO-$CaCl_2$-NaCl molten system by cyclic voltammetry with a Mo wire as the working electrode, Ni wire as the pseudo-reference electrode and graphite crucible as the counter electrode. They found that the addition of 0.5% CaO gives rise to the doubling of the Ca^{2+} deposition, with the first deposition coming from CaO and the second coming from $CaCl_2$ with the reductive peak potentials at −2.15 V and −1.51 V, respectively. They speculated that 0.5% CaO gives rise to the underpotential deposition of the molten salt and hence weakens the electrochemical stability of the $CaCl_2$-based melts. Thus, their studies suggest that it can be assumed that Ca^{2+} from CaO is deposited under potentiostatic electrolysis prior to the decomposition of the electrolyte. Indeed, the applied cell voltages in the FFC process are always 2.6–3.2 V, higher than the decomposition voltage of CaO. However, it is still difficult to experimentally prove the decomposition behaviour of CaO.

In the deoxidization process, once the oxide ion is expelled from the oxide lattice, it will migrate across the electrolyte to the anode where the oxide ion is discharged and released in the form of carbon oxides [19]. Thus, the O^{2-} concentration in the electrolyte determines the maximum rate of oxide ion transport. Schwandt et al. have studied the effect of calcium oxide content on the direct electrochemical reduction of TiO_2 [23] and Cr_2O_3 [24] under cathodic potentiostatic electrolysis using a three-terminal cell that uses TiO_2 and Cr_2O_3 oxides as the cathode in addition to a graphite pseudo-reference electrode. The results demonstrated that too early an application of large cathode potentials decreases the calcium oxide (or say, O^{2-}) content of the electrolyte and imposes a kinetic limitation on the oxide ion transfer from the cathode to the anode. The lowering of oxide ion concentration leads to a longer electrolysis process and the slower deoxidization rate. They also concluded that in order to mitigate any mass transfer limitation that arises from the shortage of oxide ions, the dissolved calcium oxide concentration needs to be sufficiently high in order to allow a high oxide ion transfer rate, facilitating the cathodic reduction kinetics and precluding anodic chlorine formation that may occur if the oxide ion is absent [25]. Moreover, the reduction of $CaTiO_3$, an intermediate that is inevitably formed via the rapid incorporation of TiO_2 with Ca^{2+} and O^{2-} from the electrolyte, could release calcium ions and oxide ions back into the electrolyte so that the oxide content of the electrolyte reverts to higher values [16,25]. Based on the results, it is plausible to assume that the oxide ion concentration should remain at comparatively high values that can sustain the easy O^{2-} transport in the electrolyte. However, our earlier findings reveal that manual addition of too low or too high a CaO content into the electrolyte shows an adverse effect on the deoxidization [26]. The optimized CaO addition amount in equimolar $CaCl_2$-NaCl molten salt is suggested to be 1% by molar. On the other hand, the deoxidization of $CaTiO_3$ is believed to proceed very slowly in the reduction process even though small amounts of CaO are intended to regulate the O^{2-} transport. Further investigations are still required to elucidate the complex influence of CaO on the reduction rate, particularly the reduction of $CaTiO_3$.

To identify the effect that CaO plays in electrolysis carried out in molten salt, experiments were performed using an ilmenite bulk pellet as the cathode, a graphite rod as the anode and equimolar $CaCl_2$-NaCl molten salt with the addition of 0–2 mol% CaO as the electrolyte. The decomposition behaviour of CaO was also studied by inspecting the reduction of another ilmenite powder sample that was positioned near the cathode but was not connected to the cathode until the end of electrolysis.

2. Experimental section

2.1. Preparation of electrolyte

The electrolyte was prepared using the as-received analytical grade anhydrous $CaCl_2$ (C110766, Aladdin), NaCl (C111533, Aladdin) and the two mixed salts in a molar ratio of 1:1. The mixtures were placed in an Al_2O_3 crucible (A2590, Aladdin) with an inner diameter of 57 mm, external diameter of 63 mm and depth of 75 mm and transferred into a vertical quartz tube reactor under argon (analytical grade, >99.999%) atmosphere. The mixtures were heated to 900 °C and melted to form a molten salt. Throughout the experiments, the total mass of the electrolyte was kept at 105 g. Prior to the experiments, pre-electrolysis was carried out at 2.8 V for 6 h at 900 °C with a graphite anode (G103921, Aladdin) with a diameter and length of 6 mm and 180 mm, respectively, and a molybdenum net cathode (Shanghai G&T Hardware Co., Ltd. Shanghai, China) with dimensions of 30 mm × 10 mm in order to remove the redox-active impurities remaining in the salts. After pre-electrolysis, 0.35 g, 0.7 g, 1.05 g, and 1.4 g of CaO (C100069, Aladdin) were added to the electrolyte to constitute the 0.5, 1, 1.5 and 2 mol% components in the equimolar $CaCl_2$-NaCl molten system.

2.2. Constant cell voltage electrolysis

Constant cell voltage electrolysis was conducted under 3.2 V in