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Direct electrolytic preparation of chromium metal in $CaCl_2$−NaCl eutectic salt

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Abstract: The electro-reduction of chromium oxide (Cr_2O_3) was investigated in an equimolar mixture of $CaCl_2$−NaCl molten salt at 800 °C for developing a more efficient process for chromium preparation. Cyclic voltammetry and potentiostatic electrolysis were used to study the electro-reduction of the Cr_2O_3-loaded metallic cavity electrode. In addition, a number of parameters affecting the rate and extent of Cr_2O_3 electrolysis were considered to better understand the electrolysis process. The results demonstrate that $CaCl_2$−NaCl molten salt is applicable for preparing Cr directly from Cr_2O_3 and the electrolysis parameters exert great influence on the cathode product. Under optimal experimental conditions, nodular Cr with an oxygen content of 0.5% (mass fraction) was obtained without any chromium carbides detected by XRD. Furthermore, the relatively high solubility of CaO and quite rapid crystal growth result in the formation of large platelet $CaCr_2O_4$, and the addition of NaCl to $CaCl_2$ results in several variations on the electrolysis process and the product morphology from pure $CaCl_2$ molten salt.
Key words: electrolysis; chromium; chromium oxide; $CaCl_2$−NaCl molten salt

1 Introduction

Chromium (Cr) metal is an attractive engineering material for many areas of applications owing to its properties of high melting point and considerable corrosion resistance [1,2]. Cr metal is predominantly produced by aluminothermic reduction of Cr_2O_3 at high temperature above the melting point of Cr. The other process is to use CrO_3 aqueous electrolyte electrolysis. However, the side reactions, chiefly the redox cycling of the multi-valence chromium ions (mainly Cr^{2+}, Cr^{3+} and Cr^{6+}) and Cr^{3+}/Cr electrode potential being more negative than that of H^+/H_2, account for the low current efficiency and the hydrogen brittleness [3]. In addition, there are laboratory studies about Cr electro-deposition from expensive $CrCl_2$, $CrCl_3$ or K_3CrF_6 in molten salt [3−5].

The FFC-Cambridge process, based on the concept of cathodic oxygen ionization of solid oxide in $CaCl_2$-based molten salt, has been demonstrated for the successful preparation of metals and alloys, such as titanium [6−9], niobium [10,11], tantalum [12,13], silicon [14], germanium [15], zirconium [16,17], $CeCo_5$ [18], and $ZrMn_5$ [19]. Particularly, researchers have validated the feasibility of the electro-reduction of Cr_2O_3, and a series of experiments have been performed to determine the influence of the electrolysis time, electrolysis voltage and anode areas on the electrolysis process in $CaCl_2$ molten salt [1,2,20]. However, pure $CaCl_2$ has a high melting point of 782 °C, hence, resulting in the electrolysis temperature as high as 900−950 °C. Moreover, chromium carbide was detected after Cr_2O_3 electrolysis due to the high temperature and high solubility of O^{2-} in $CaCl_2$ molten salt [20,21]. A process is always desired if it can proceed without external heating or at a lower temperature, if heating is inevitable, because of its relative energy-saving, mild reaction conditions and reduced corrosion property [10]. Substitutional $CaCl_2$-based electrolyte with low melting temperature has been selected to perform the FFC

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process. For instance, it is demonstrated experimentally that $CaCl_2$−NaCl eutectic salt as the electrolyte is available and could be applied to preparing Nb [10], Ta [12], Ge [15], and U [22]. The addition of NaCl or other alkali or alkaline earth chloride to $CaCl_2$ may affect the electrolysis of solid oxide in several manners: both desired and undesired [2]. GORDO et al [2] reported that $CaCl_2$−NaCl molten salt is expected to have a lower capability to accommodate O^{2-}, leading to a lower background current and alleviative graphite corrosion.

Herein, the equimolar mixture of $CaCl_2$ and NaCl was selected as the molten salt. CVs and potentiostatic electrolysis of Cr_2O_3 in $CaCl_2$−NaCl molten salt were investigated. Experimental work was also undertaken to study the influence of process variables on the extent and rate of electro-reduction of Cr_2O_3. Particular attention was paid to the role of Ca^{2+} and Na^+ involved in the formation of intermediate product, because intermediate $Ca_xM_yO_z$ (M means metal) was often detected, whereas $Na_xM_yO_z$ was rarely found during the electrolysis of metal oxides in $CaCl_2$−NaCl molten salt [10,12,15,22]. Finally, the influence of $CaCl_2$−NaCl and pure $CaCl_2$ on the electrolysis process and the product morphology was compared.

2 Experimental

Cr_2O_3 (>99%, mass fraction) powders of 1.5 g were compressed into compact cylinder pellet with a uniaxial pressure of 170 MPa in a 13 mm diameter steel die. These pellets were subsequently sintered at a specific temperature for 3 h. The porosity of the as-sintered pellet was measured by the Archimedes method. The sintered pellets were then drilled, connected into a current collector and assembled as an oxide cathode. Anhydrous $CaCl_2$ (>96%, mass fraction) and NaCl (>99.5%, mass fraction) were blended with mole ratio of 1:1 in alumina crucible (99%, mass fraction). The details of the preparation for the electrolyte were described in Ref. [10].

CV curves of Cr_2O_3 in $CaCl_2$−NaCl molten salt were recorded using the metallic cavity electrode (MCE) according to Ref. [23], with a computer-assisted solartron electrochemical workstation employed. Cr_2O_3 powders were manually pressed into the cavity of the MCE, which functioned as working electrode during CV test. A graphite rod and Ag/Ag^+ electrode (10% AgCl, 45% NaCl and 45% KCl in mole fraction, sealed in alumina pipe) were used as the counter and reference electrodes, respectively [24]. The CV tests were conducted with a scan rate of 100 mV/s, with the potential ranging from 0 to −1.8 V (vs Ag/Ag^+). Potentiostatic electrolysis was performed at −1.4 V (vs Ag/Ag^+) using MCE loaded with Cr_2O_3. After potentiostatic experiment for 300 s, the Mo/Cr_2O_3 sample was retrieved, washed with dilute HCl solutions and dried.

The electrolysis of solid Cr_2O_3 was performed in a sealed stainless steel reactor, in which the center was located in the alumina crucible holding the molten salt. A high-density graphite rod of 15 mm in diameter was used as the anode. Both the anode and cathode current collectors were enclosed by an alumina pipe for insulation. The cell was flushed with argon while it was heated to the required temperatures and kept leak-proof to maintain an inert atmosphere of high purity argon gas. On reaching electrolysis temperature of 800 °C, the pre-electrolysis of the thermally dried molten salt was conducted using a constant voltage of 2.0 V applied between the graphite anode and stainless steel cathode to remove the residue moisture and metallic impurities from the electrolyte. After pre-electrolysis, Cr_2O_3 electrode was inserted into the molten salt and a constant voltage varying from 2.5 to 3.2 V was imposed between the anode and oxide cathode with approximately 30 mm apart from each other. The graphite anode was immersed to a salt depth of 3 cm corresponding to a geometric surface area of 16 cm^2. After a predetermined time, the electrolysis was terminated and the cathode was quickly lifted above the molten salt, cooled in argon atmosphere to room temperature and removed from the reactor. These recovered pellets were subsequently washed with distilled water to remove the solidified salt. They were further rinsed with dilute HCl solutions with pH 3. Such vigorous procedure could confirm that all the salts attached on the pores of the pellets could be eliminated from the electrolysis product. Finally, the sample was dried in a freezer dryer.

The microstructural composition of the sintered or electrolyzed pellet was observed using a scanning electron microscope (SEM) coupled with an energy-dispersive X-ray analysis (EDXA) attachment. Various phase compositions present in the prepared samples were determined by X-ray diffraction (XRD) with the scan range set from 10° to 90° after grinding the pellet. The oxygen content was determined by pulsed infrared melting−infrared thermal conductivity detection analysis (PIM−ITC).

3 Results and discussion

3.1 Electrochemical test

$CaCl_2$−NaCl eutectic salt with mole ratio of 1:1 has a low melting point of 504 °C, whereas most-frequently used $CaCl_2$ has a high melting point of 782 °C, thus giving the eutectic salt potential to be employed at a lower working temperature. Table 1 illustrates the theoretical electrode potentials of Cr_2O_3, $CaCl_2$ and NaCl