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SYNTHESIS OF CHROMIUM AND FERROCHROMIUM ALLOY IN MOLTEN SALTS BY THE ELECTRO-REDUCTION METHOD

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Abstract

In this work, we successfully applied the Fray-Farthing-Chen Cambridge electro-reduction process on the preparation of chromium from chromium oxide, and for the first time, the synthesis of ferrochromium alloy from chromium oxide and iron oxide mixture and the chromite ore in molten calcium chloride. The present work systematically investigated the influences of sintered temperature of the solid precursor, electrochemical potential, electrolysis temperature and time on the products by using a set of advanced characterization techniques, including XRD and SEM/EDS analyses. In particular, our results show that this process is energy-friendly and technically-feasible for the direct extraction of ferrochromium alloy from chromite ore. Our findings thus provide useful insights for designing a novel green process to produce ferrochromium alloy from low-grade chromite ore or stainless steel slag.

Keywords: *Ferrochromium; Molten salts; FFC Cambridge Process; Electrochemistry*

1. Introduction

As is well known, chromium is frequently used in most alloy steels and nonferrous high-performance alloys for various purposes, such as aerospace applications. However, the chromium produced by the traditional Goldschmit process [1-3], always contains multiple impurities, including un-reacted aluminum, and some intermetallic compounds. Preparation of high-purity chromium can be carried out in aqueous solution or molten salts by the electrochemical methods, but these processes often have low current efficiencies, high energy consumption and also may lead to serious environmental pollution especially when dealing with Cr(VI) [4]. Ferrochromium (CrFe) is also of central importance for high-quality alloy steel production, which is predominantly produced by the carbon reduction process. Since thermodynamically the formation of different chromium carbides are more favorable than chromium, the product is actually carbon ferrochromium, such as $(Cr, Fe)_{23}C_6$, $(Cr, Fe)_3C_2$, $(Cr, Fe)_7C_3$. The high energy burden, adverse environmental consequences, a huge amount of waste slag, and the low quality of product, make this process gradually unacceptable.

In the past decade, a novel electro-reduction method, namely Fray-Farthing-Chen (FFC) Cambridge process, was proposed for the direct extraction of metal and alloy from its corresponding oxides [5,6]. This process is able to strip away the oxygen by the electrochemical reduction occurring in a molten salt media (typically $CaCl_2$), thus leaving the oxygen-free metal/alloy at the cathode, it often involves the investigations regarding the electrochemical behaviors of metal ions in the molten salts [7]. The method is found to be very efficient in energy-saving, and is clearly environment-friendly since it emits only oxygen when using the inert anode (or CO/CO_2 from the graphite anode). This revolutionary method has been widely applied for the production of a diversity of metals and alloys [8-11], such as Ti, Cr, Nb, Si, $TbNi_5$, Nb_3Sn, Ti-10W, etc. Prior studies show that the extraction of metal/alloy via this process route from sulfides was feasible as well [12,13]. On the other hand, another electrochemical process - Salt Extraction Technique (SET) was also proposed recently [14-18], and was

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applied for the electrowinning of chromium and ferrochromium [14]. However, no earlier study was carried out for the synthesis of ferrochromium via the FFC route. This study aims to explore the preparation of Cr and CrFe alloy by the FFC process, particularly focusing on the later one. Influences of sintered temperature, electrolysis time and temperature on the product are systematically investigated.

2. Experiments

2.1. Thermodynamic Principles

The cathode and anode reactions of this process can be briefly described below:

$$\text{Cathode: } MO_{x(Solid)} + 2xe = M_{(Solid)} + xO^{2-} \quad (1)$$

$$\text{Anode: } xO^{2-} - 2xe = (x/2)O_2 \text{ (inert anode)}$$

$$\text{or } O^{2-} - 2e + C = CO \text{ or } 2O^{2-} - 4e + C = CO_2 \text{ (graphite anode)} \quad (2)$$

Where MOx refers to the metal oxide or the mixture of metal oxides. The overall reaction using a graphite anode can be summarized as follows:

$$MOx + xC = M + xCO \quad \text{or}$$

$$MOx + (x/2)C = M + (x/2)CO_2 \quad (3)$$

The cell potential can be estimated from ΔG_T^θ value of the corresponding oxides using the Nernst equation. At 900°C, the theoretical decomposition voltages for Cr_2O_3, Fe_2O_3 and $CaCl_2$ are calculated to be 0.94V, 0.59V and 3.33V, respectively. The cell voltages for reduction of Cr_2O_3 and Fe_2O_3 in $CaCl_2$ salt should be below the decomposition voltage of $CaCl_2$.

The actual potentials in a real system deviate from these values because of the system resistance and/or the varying activities of the reactants, we chose 2.8V~3.0V, which is enough for the following trials.

2.2. Materials and experiments

Anhydrous $CaCl_2$ (TianJin YongDa Chemical Reagent Company, > 97 wt%) was dried at 300 °C for at least 48 hours and kept in an oven at 160 °C before use to remove the moisture. Cr_2O_3 powder (TianJin Chemical Reagent Company, 99.99 wt% Cr_2O_3), combined with PVA binder, was pressed into pellets with the diameter of 12 mm and weight of ~1.5 g at a pressure around 1750 kg/cm^2. The pellets were sintered in air at 950 °C and 1150 °C for 2 hours, respectively. Similar procedure was repeated for mixed (1:1 mole ratio) Cr_2O_3 and Fe_2O_3 powder (Beijing NanShangLe Chemical Engineering Company), except for some mixture pellets sintered at 1350 °C. A special mould was used to introduce an iron wire though the center of Cr_2O_3 pellet. The chromite powder was also pressed into pellets at a pressure around 10 MPa, and sintered at 950 °C, 1150 °C and 1350 °C in air for 3 hours, respectively. Each mixture or chromite pellet is about ~2g and 10 mm diameter. We used a thin iron wire (1 mm diameter) to wrap the pellet, and they were stored in an oven around 110 °C before attaching to an iron rod (5 mm diameter) as the cathode lead.

Graphite rod (5 mm diameter) was used as anode in this study. A DC power supply (DH1718E-4 Beijing Dahua Equipment Company) was employed. 99.99 % argon gas (AGA gas AB, Sweden) was used as the protective gas, and the silica gel was used to remove moisture in the gas flow. The temperature was controlled by a FP93 temperature controller. Alumina crucible (40 mm OD, 36 mm ID, 60 mm height from KERANOVA AB, Sweden) were employed as the reaction vessel, and they were heated in an oven at 110 °C for about 1 hour before use.

The crucible, with a thermocouple under its bottom, was filled with $CaCl_2$ and placed inside an alumina tube sealed with rubber stoppers. The entire assembly was heated by a programmed heating procedure: the reactor was slowly heated to 300 °C with a rate 1~2 °C/min, held for 3 hours, heated with a rate of 4~8 °C/min to the target temperature, kept at this temperature for 0.5~1 hours to ensure the homogeneity, and then the electrodes were inserted into the melt. A cell voltage 0.5V was applied for 0.5~1 hours. After that a suitable cell voltage was charged for electrolysis as prescribed. The change of current during electrolysis was recorded.

After electrolysis, the electrodes were held above the molten salts and cooled down upon the argon flow. The cathode was washed with distilled water and subjected to sonication. For chromium, diluted HCl solution was used, ethanol was used for ferrochromium alloy. The reduced pellet was dried at 60~110 °C quickly and stored in a desiccator before analysis. The samples were analyzed by X-Ray Diffraction technique (Rigaku DMAX-RB 12Kw rotating anode X-ray diffraction instrument), and LED-1450 scanning electron microscope(SEM) equipped with Energy Dispersive X-ray Spectrometry(EDS) analysis.

3. Results and Discussion

3.1. Electrochemical reduction of Cr_2O_3

Figure 1 displays the SEM photos of not-sintered and 950 °C and 1150 °C sintered pellets in air for 2 hours, respectively. Clearly, the particles grow bigger after sintering. 1150 °C sintered pellet has cubic-like particles without rhombus ones, larger and more homogeneous than the one sintered at 950 °C, which is beneficial for the transportation of oxygen ions. As shown in Figure 2, 1150 °C sintered pellet can be reduced completely after 4 hours, while the 950 °C sintered one was only partially reduced after 4h electrolysis.

Another finding observed in Figure 2 is the intermediate product identified as calcium chromate,

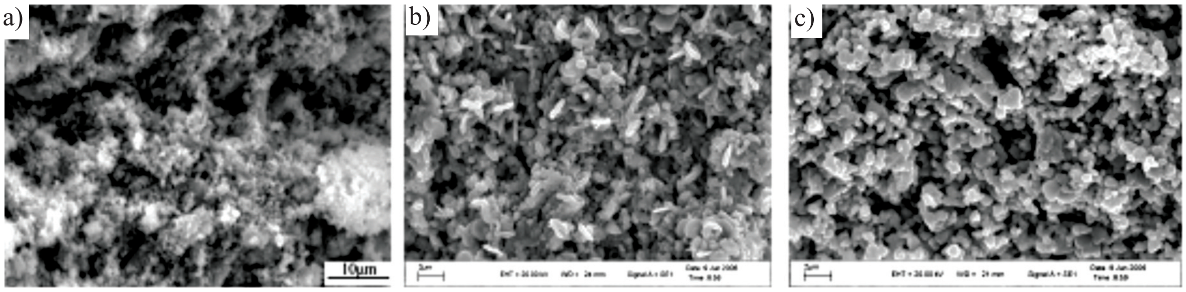

Figure 1. *SEM morphologies of Cr_2O_3 pellets before electrolysis (a) not-sintered, (b) sintered at 950°C, (c) sintered at 1150°C*

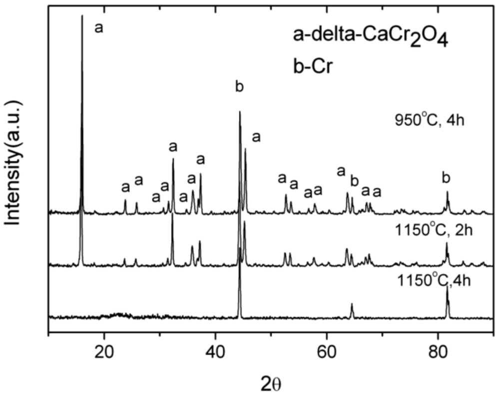

Figure 2. *XRD patterns of the products for Cr_2O_3 pellets after electrolysis at 900°C and 3.0V*

which can be seen from the SEM image directly. Figure 3a presents a typical image of outside layer for 1150 °C sintered pellet after 2h electrolysis, showing two distinct microstructures, cubic-like and flower-like grains respectively. EDS analysis indicates that the cubic-like grain is pure chromium (> 99 %), while the flower-like grain contains Ca, Cr, O and a low content of Cl. The ratio of Ca, Cr and O is close to 1:2.3:3, suggesting the presence of calcium chromate. In fact, with the progressed discharge of oxygen ions during electrolysis, different stoichiometric calcium chromate, $CaCr_xO_y$, can be formed and finally transit into the chromium metal, as shown by the cubic-like microstructure in Figure 3b, for a completely reduced pellet.

Longer electrolysis time is better for de-oxidation, however since the graphite anode is consumable, longer time may induce unfavorable effects. For the 1150 °C sintered pellets, after electrolysis for 6h and 8h at 900 °C/3.0V, $Cr_{23}C_6$ or Cr_7C_3 are found in the XRD analysis. The carbon particles can drop off, even cover the entire top surface of molten salt in a lab-scale cell, resulting in short-circuit, which can consume a large amount of power but output nothing, thus significantly reduce the current efficiency. For example, we found that the current efficiency for 4h electrolysis of 1150 °C sintered pellet is estimated to be only 38.8 %. Utilization of a membrane between electrodes or inert anode is likely helpful to increase the current efficiency, which is the subject of our future work.

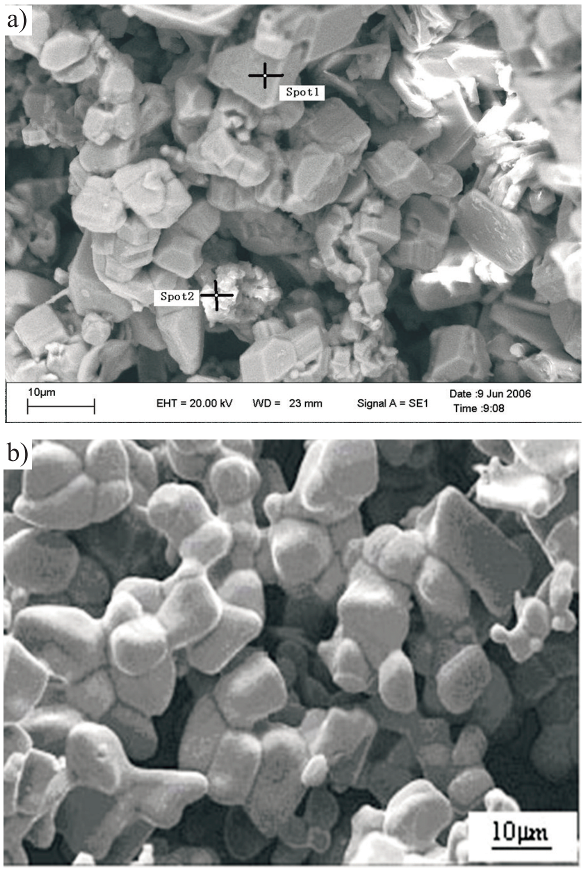

Figure 3. *SEM images of reduced products. (a) 4h electrolysis of 1150 °C sintered Cr_2O_3 pellet (b) 10h electrolysis of 1150 °C sintered Cr_2O_3-Fe_2O_3 pellet*

3.2. Electrochemical reduction of Cr_2O_3-Fe_2O_3

Cr_2O_3 and Fe_2O_3 powder were mixed as 1:1 mole ratio to mimic the chromite ore, and the pellet was also sintered at a higher temperature of 1350 °C. Though the 1350 °C sintered pellet does show much bigger particles than the 1150 °C one (Figure 4), it does not represent a significant improvement of the electrochemical reduction behavior. The XRD results of 1150 °C and 1350 °C sintered pellets after 6h electrolysis were essentially the same. A possible reason is that although bigger particles enlarge the voids between neighborhood particles, favorable for the penetration of calcium chloride and transportation of oxygen ions, it also makes the diffusion of oxygen ions inside the big particles to the salt phase more difficult. Thus, we prefer the sintered temperature of 1150 °C.

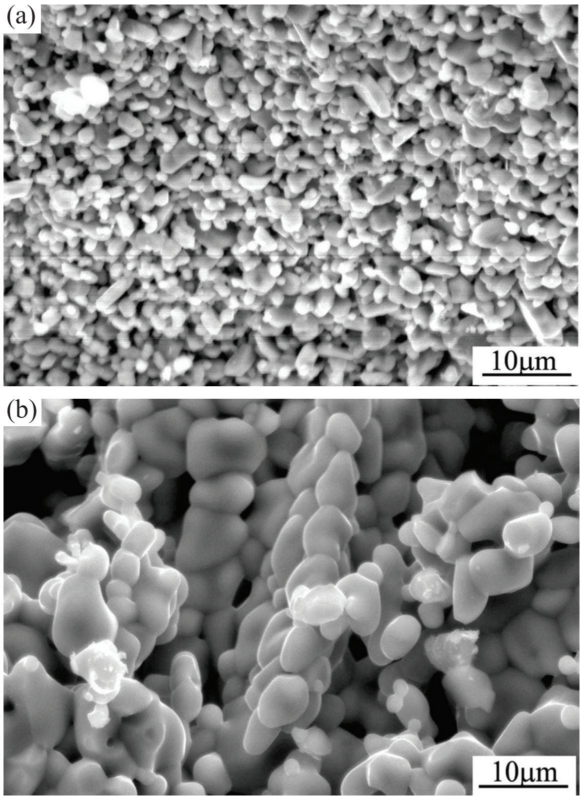

Figure 4. *SEM morphologies of the pellets before electrolysis (a) sintered at 1150 °C, (b) sintered at 1350 °C*

Figures. 5 and 6 present the SEM/XRD results of reduced 1150 °C sintered pellets. After 10h electrolysis, the reduction was complete while after 6h electrolysis, calcium chromate still existed, as shown in Figure 6 and the flower-like structure in Figure 5a.

It should be noted that no intermediate products containing iron were found during 900 °C electrolysis, which means that Fe_2O_3 was first and very quickly reduced. This can be expected from the lower theoretical decomposition voltage of Fe_2O_3 than Cr_2O_3. One may wonder the longer time for mixed Cr_2O_3/Fe_2O_3 pellet required than that needed for the completedeoxidation of chromium oxide, actually, it is caused by the low current level during electrolysis of Cr_2O_3-Fe_2O_3.

The current efficiency is estimated to be 33 %, for 10h electrolysis of 1150 °C sintered Cr_2O_3-Fe_2O_3 pellet at 900 °C and 3.0V, a bit lower than 38.8 % for 4h electrolysis of 1150 °C sintered Cr_2O_3 pellet. XRD result for the pellet after 8h electrolysis at 900 °C/3.0V actually contained a very low amount of calcium chromate indicating the current efficiency should be higher than 33 %, essentially at the same

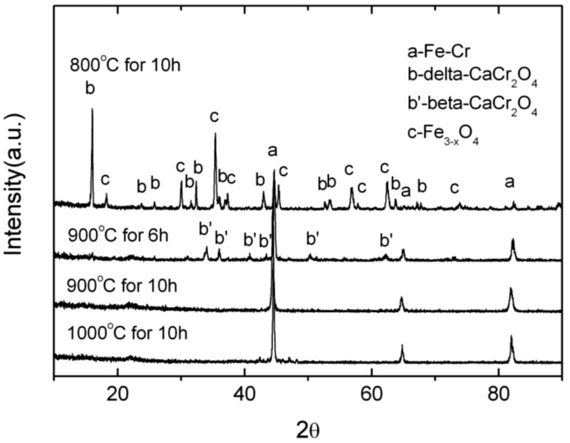

Figure 6. *XRD patterns of the products for 1150 °C sintered pellet at different electrolysis temperatures and time*

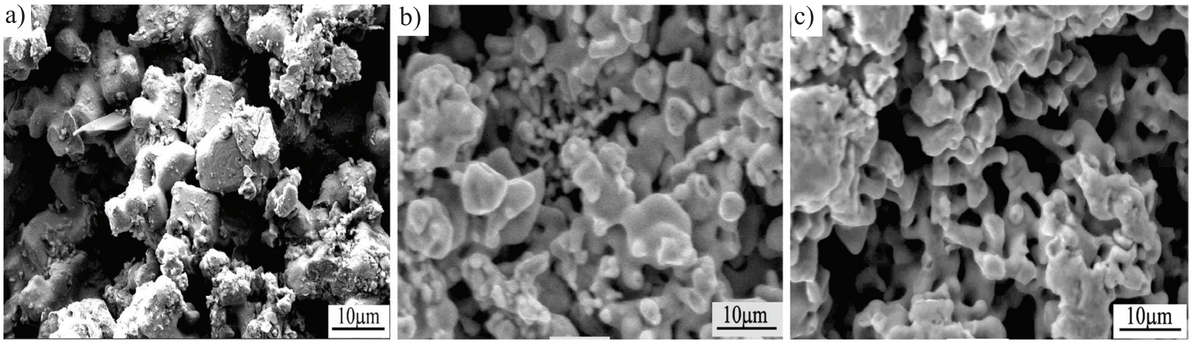

Figure 5. *SEM morphologies of the reduced 1150 °C sintered pellets. (a) 6h electrolysis at 900 °C and 3.0V (b) 10h electrolysis at 900 °C and 3.0V (c) 10h electrolysis at 1000 °C and 3.0V*

level as it does for Cr_2O_3 reduction.

Temperature can affect the surface tension, viscosity of the molten salts, which are important for the transportation of oxygen ions. As shown in Figure 6, the pellet was only partially reduced after 10h electrolysis at 800 °C, even with some un-reduced iron oxides. Although electrolysis at 1000 °C for 10h can accomplish a complete reduction, heavy evaporation of $CaCl_2$ and more graphite particles dropped from the anode on the molten salt surface were observed. We also found that the reduced pellet become very brittle may increase the loss of reduced products into the bulk molten salts during electrolysis. Thus, 900 °C is preferred for electrolysis.

Figure 7 shows a cross-section of a partially reduced product. Along the radial direction, inside layer is dense, medium layer is looser with grey color and the outside layer represents a metal color. SEM/EDS and XRD results shows that inside layer is comprised of CrFe, calcium chromate and other metal elements, such as Mg, Al, Si, Ca, Cl; medium layer contains CrFe and calcium chromate with a very low content of impurities; outside layer is completely CrFe alloy, no other elements are detected. This finding suggests the following mechanism: The surface and the center part of the pellet are metalized quickly via the metal wire, and then the metal-oxide-electrolyte interline starts to proceed from outside to inside, and from inside to outside; since the contact area with electrolyte of outside interline is much larger than the inside one, the outside interline progresses much faster, which is likely the reason of higher content of calcium chromate in the inside layer than in outside layer; finally, when the two interlines meet each other, the pellet is reduced completely.

This reduction pathway can be observed from the typical current-time plot, as shown in Figure 8a for Cr_2O_3 reduction. The initial peak corresponds to the metallization of the pellet surface since the oxygen ions in a thin metal layer are very easy to diffuse to the bulk electrolyte. Once the surface metallization is completed, the current decreases to a plateau corresponding to the slow propagation of metal-oxide-electrolyte interline. When the reduction is completed, the current drops down to another plateau. It is necessary to hold electrolysis on this background current to obtain a high-purity metal or alloy product, yet it is also important to make this current as low as possible, so as to reduce the non-profitable energy consumption.

However, no obvious current peak is observed for electrolysis of Cr_2O_3-Fe_2O_3 (Figure 8b). In our opinion, for a Cr_2O_3-Fe_2O_3 pellet, there are two possible metal-oxide-electrolyte interlines for iron and chromium, respectively. First, the reduction of Fe_2O_3 proceeds very fast and leads to the fast surface metallization without a clear current peak. The iron-oxide-electrolyte interlines progresses though the entire pellet in a very short time, and the reduction then focuses on oxygen removal from Cr_2O_3. Probably, the electric conductivity of the partially reduced pellet, like Cr_2O_3 embedded in an iron-

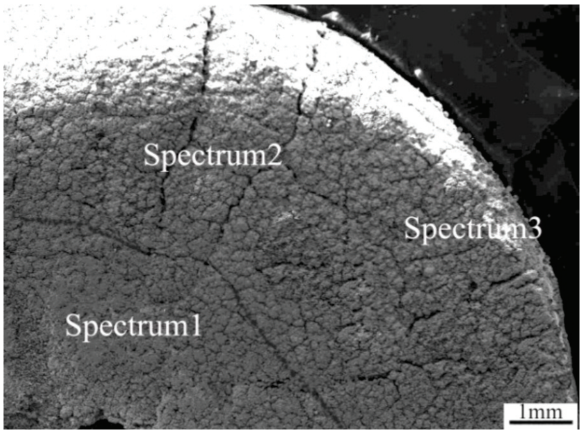

Figure 7. *Cross-section of a partially reduced 1150 °C sintered Cr_2O_3-Fe_2O_3 pellet after 8h electrolysis at 900 °C and 3.0V*

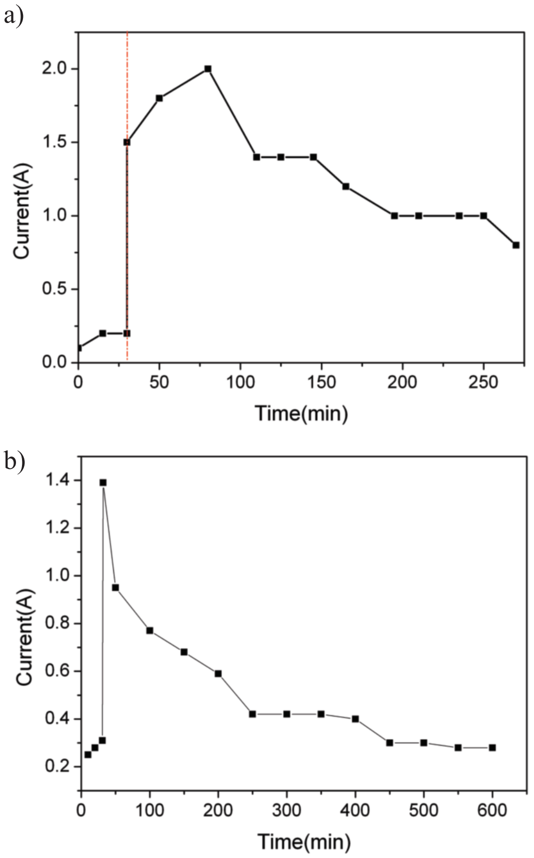

Figure 8. *Typical current-time plots during electrolysis (initial low current is recorded at 0.5V). (a) 4h electrolysis of 1150 °C sintered Cr_2O_3 pellet (b) 10h electrolysis of 1150 °C sintered Cr_2O_3-Fe_2O_3 pellet*

network, is lower than the metalized layer during electro-reduction of chromium oxide. Therefore, a low current level was observed, and most of the oxygen ions transportation from chromium oxide to the bulk salt phase occurs at this low current plateau. Consequently, a longer time is required for a complete reduction. Similar phenomenon was observed for preparation of $TbNi_5$ [19] supports this proposed pathway.

Table 1. *Composition of chromite (wt%)*

Fe	Cr	Si	Mg	Al	Ni	Ti	Cu	Ca	Zn
23.4	37.1	6.9	6.7	9.0	0.2	0.2	0.2	0.4	0.3

3.3. Electrolytic reduction of chromite ore

The chromite ore can be presented as $(Fe,Mg)(Cr,Al)_2O_4$, SiO_2 is not in the spinel structure. The composition of chromite used in this work is shown in Table 1. Since other metal oxides, such as SiO_2, can be also reduced during electrolysis, careful design is necessary to obtain a high-quality ferrochromium alloy. First, a suitable cell voltage should be applied to avoid the reduction of other metal oxides; secondly, proper duration time should be used for complete reduction of Fe_2O_3 and Cr_2O_3, and the magnetic separation is expected to recover the CrFe alloy from other nonmagnetic oxides after removal of the adhered salts of the pellet.

Several preliminary experiments were carried out with a cell voltage of 2.8V at 900 °C. The XRD results are presented in Figure 9. After 4h electrolysis, we found the existence of CrFe, but the main component is still (Fe, Mg)O $(Cr, Al)_2O_3$; after 8h electrolysis, CrFe is the main component, other impurities are mainly various oxides but in very low contents. This result proves the feasibility of using FFC method to extract ferrochromium alloy directly from chromite. Future work will focus on the separation of impurities during and after electrolysis.

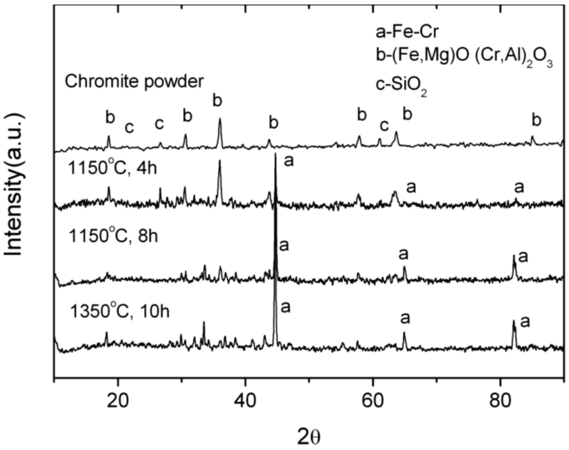

Figure 9. *XRD results of the products for chromite pellets sintered at different temperatures*

4. Conclusions

In this work, direct electrochemical preparation of chromium and ferrochromium powder was carried out in molten $CaCl_2$. First, the chromium is successfully obtained after 4h electrolysis of Cr_2O_3 pellet. Calcium chromate was found as an intermediate product during electrolysis. For the reduction of Cr_2O_3-Fe_2O_3 pellet, 1150 °C sintered temperature and 900 °C electrolysis temperature are better to improve the electrochemical properties of the pellets. In this work, the current efficiency for preparation of chromium or ferrochromium alloy is ~40 %, and the graphite particles dropped from the anode heavily decreased the current efficiency. From the analysis of a partially reduced product, combining with the current-time plots, we demonstrate the reduction pathway of an oxide pellet. Furthermore, the preliminary investigations from the direct reduction of chromite was promising, after 8h electrolysis of a 1150 °C sintered pellet, the main component of the product is CrFe alloy, with low contents of oxide impurities.

Acknowledgements

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