Short Communication

Pulsed Current electrodepostion of manganese in NaCl-KCl-MnCl$_2$ melt

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Pulsed current electrolysis was applied in NaCl-KCl-MnCl$_2$ melt at 983 K to enhance morphology of cathode product. A tungsten wire was used as the working electrode, a carbon rod was employed as the counter electrode and Ag/AgCl was used as the reference electrode. The electrochemical reduction of Mn^{2+} was investigated in this three-electrode cell. Then tungsten wire and carbon rod were used as the cathode and anode to establish a two-electrode cell. Under pulsed current electrolysis, the influence of various pulsed parameters (e.g., periodic time (t) and the ratio of t$_{on}$ to t$_{off}$ (n)) on the morphology of cathode product was explored. It was found that comparing with that of direct current electrolysis, when t=10 min, n=1, the produced manganese with coarser grain was obtained. In addition, high carbon ferromanganese was used as the anode, with a tungsten plate as the cathode to perform pulsed current electrorefining. It was also concluded that when t=10 min, n=1, the morphology of produced manganese and iron was obviously improved, with large grain obtained.

Keywords: high carbon ferromanganese, manganese, pulsed current electrolysis, molten salt

1. INTRODUCTION

Manganese is an important alloying agent in iron and steel industry. With the development of high-Mn (10-30 wt %) and high strength automotive steel [1], the requirement for pure manganese metal is also increasing. Due to the expensive cost and environmental pollution for the current process of manganese preparation [2,3], it is suggested that pure ferromanganese could replace the pure manganese as an alloying agent in steel manufacturing. Norwegian University of Science and Technology [4] and the TU Clausthal in Germany and Siemens VAI Technology Co., Ltd. [5] have carried out studies on producing low-cost and pure ferromanganese. On the other hand, decarburization process of high carbon

ferromanganese has been used to prepare low carbon ferromanganese alloys for a long time [6-9]. However, in this process there is a significant amount of manganese left in slag, leading to high energy consumption and low metal yields. Therefore, it is necessary to develop a new process to produce pure ferromanganese at low cost.

In recent years, the authors [10] applied high carbon ferromanganese as a feeding material and produce manganese and iron successfully by molten salt electrorefining. However, it is difficult for the produced refractory manganese and iron to be recovered due to their powdery morphology and they tends to be oxidized easily. Pulsed current electrolysis is an alternative technique to enhance the morphology of the cathode deposits [11-14]. The authors have found that the cathode process of Mn^{2+} in NaCl-KCl mixture was determined as diffusion-controlled [15], so the morphology of manganese in this electrolyte could be improved by pulsed current electrolysis. In this paper, in molten NaCl-KCl-$MnCl_2$ electrolyte at 983 K, pulsed current electrolysis was employed to enhance the morphology of cathode product.

2. EXPERIMENTAL

NaCl and KCl (analytical grade) were used as the electrolyte, which were dried at 473K for more than 48 h to remove the surface moisture in a drying oven. They were mixed with the eutectic ratio (59.6:49.4 mol%) before use. $MnCl_2$ (analytical grade) was added to the mixture as an electroactive electrolyte.
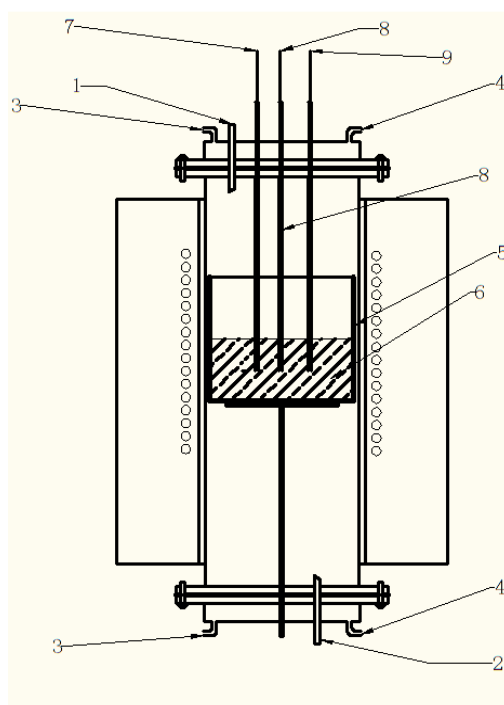

Figure 1. Experimental setup for electrochemical tests (1. argon gas inlet; 2. argon gas outlet; 3. cooling water inlet; 4. cooling water outlet; 5. alumina crucible; 6. NaCl-KCl melt; 7. reference electrode; 8. working electrode; 9. counter electrode;)

Electrochemical tests and electrolysis were carried out at a temperature of 983 K in an experimental setup as shown in fig. 1. An electrochemical cell was located in a programmable vertical furnace. The inside atmosphere was under argon gas. A tungsten wire (Φ1 mm) was used as the working electrode, a carbon rod (Φ 6 mm) was used as the counter electrode and Ag/AgCl was employed as the reference electrode. Preparation of Ag/AgCl has been described in previous work [16]. The electrolyte was contained in an alumina crucible, which was supported by a carbon supporter. The electrodes were polished by sand paper and rinsed by ethanol before being introduced to the cell. All the potentials are referred to Ag/AgCl reference electrode in the present study.

During direct and pulsed current electrolysis, a two-electrode cell was applied. A tungsten wire (Φ1 mm) and a carbon rod (Φ8 mm) were used as the cathode and anode, respectively. During the electrorefining of high carbon ferromanganese, high carbon ferromanganese ($2\times5\times40$ mm) and tungsten ($1\times10\times40$ mm) plates were used as the anode and cathode, respectively. After electrolysis, the cathode deposits were collected, with the procedures described in detail in previous work [16].

The electrochemical tests as well as direct and pulsed current electrolysis were conducted by PARSTAT 2273 potentiostat with Powersuite software (Princeton Applied Research, AMETEK). Cyclic voltammetry was used to investigate the cathode process of Mn^{2+} at a scan rate of 100 mV·s^{-1}. The phase composition and microstructure of cathode product were examined by x-ray diffraction (Bruker D8 Advance; Bruker corporation, Germany) and scanning electron microscopy (JSM-6510LV; JEOL), respectively.

3. RESULTS AND DISCUSSION

3.1 Pulsed current electrolysis in NaCl-KCl-MnCl₂ with a carbon anode

The cathode process of Mn^{2+} in molten NaCl-KCl-MnCl$_2$ (1.25×10^{-4} mol·cm^{-3}) was investigated by cyclic voltammetry. Fig. 2 (a) shows the voltammogram at a scan rate of 0.1 V·s^{-1}. Two redox couples A/A1 and B/B1 are observed. According to thermodynamic calculation, it is assumed that A/A1 corresponds to deposition and dissolution of alkali metal and B/B1 corresponds to that of manganese. The reduction of Mn^{2+} occurs at a potential of around -1.1 V vs Ag/AgCl. Subsequently, potentiostatic electrolysis was performed under a cathode potential of -1.7 V vs Ag/AgCl in a three-electrode system using NaCl-KCl-MnCl$_2$ (10 wt%) electrolyte at 983K. The cathode product was examined by x-ray diffraction, with the pattern shown in fig. 2(b). It is observed that the product is Mn metal.

Different currents were applied in NaCl-KCl-MnCl$_2$ (10 wt%) melt to investigate the effect of current density on the morphology of produced manganese. Fig. 3 demonstrates the SEM images of manganese under different current density ranging from 0.3 to 0.9 A· cm^{-2}. All the products consist of powder. The particle size decreases with the increase of the current density. Higher current density tends to cause more dendrite formation under concentration polarization [14]. When the current density is 0.3 A· cm^{-2}, the grain size of manganese is the largest. So in the sequent pulsed current electrolysis, the current density is selected as 0.3 A· cm^{-2}.
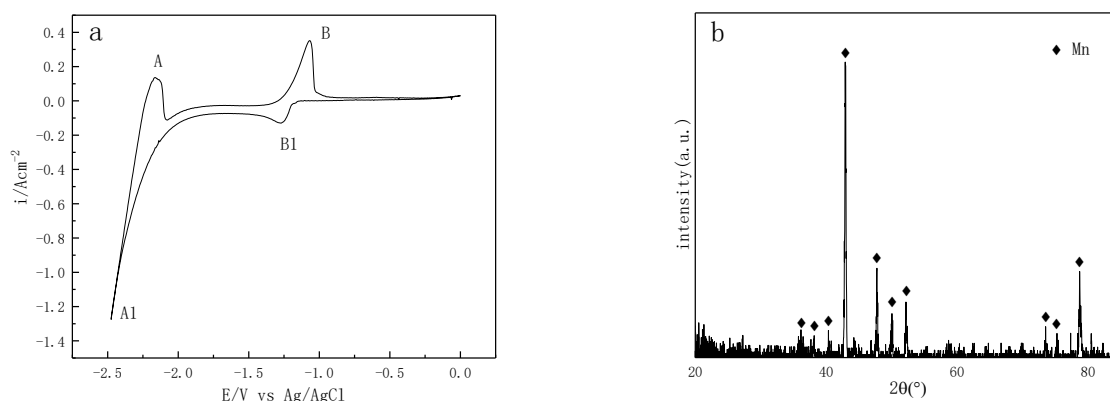
Figure 2. (a) Cyclic voltammogram on tungsten in NaCl-KCl-MnCl$_2$ (1.25×10^{-4} mol·cm^{-3}) molten salts at 983 K; (b) XRD result of cathode product under -1.7 V vs Ag/AgCl in NaCl–KCl-MnCl$_2$ (10 wt%) melt at 983 K.
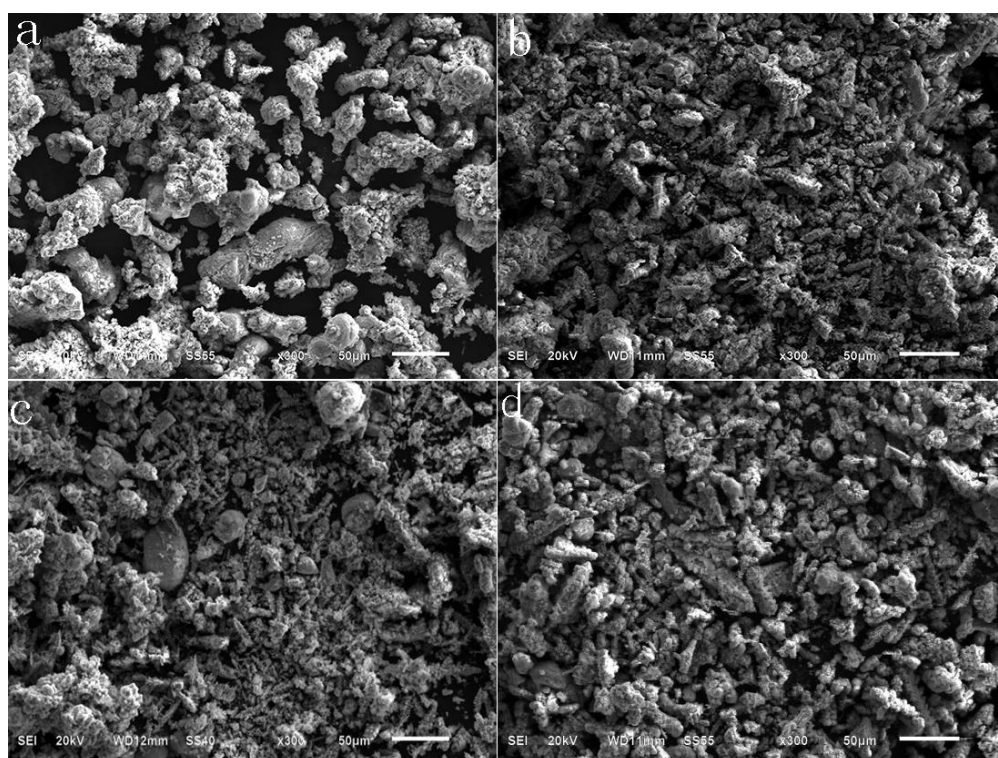

Figure 3. SEM images of manganese at various cathode current densities in NaCl–KCl-MnCl$_2$ (10 wt%) melt at 983 K.（a）0.3A·cm^{-2};（b）0.5A·cm^{-2};（c）0.7A·cm^{-2};（d）0.9A·cm^{-2}.

During the electrodeposition of solid metal, there are two parallel processes: nucleation and crystal growth. The total current consists of that of nucleation and crystal growth. If the nucleation current is more than that of crystal growth, the grain size of the deposit tends to be small.

Nucleation current corresponds to nucleation rate essentially, which is dependent on the nuclei number per unit time. The relationship [17] between nuclei number and current density as well as the concentration of metal ions is as shown in equation (1).

$$N_n = a + b \times lg[D_k/C_{me}] \qquad (1)$$

Where N_n is nuclei number, a, b are constants dependent on the properties of the metal, D_k is cathode current density and C_{me} is the concentration of metal ions in the bath.

During the initial stage of electrolysis, the concentration of metal ions in the vicinity of an electrode is as large as the bulk concentration. According to equation (1), the nuclei number is small, leading to cathode product with coarse grain. As the electrolysis proceeds, metal ions are consumed in the vicinity of the electrode and the mass transfer of them cannot match the reduction rate due to their slow diffusion, resulting in lower concentration of metal ions on the electrode surface. Thus a large amount of nucleation was generated and cathode product with small particle size is obtained. Therefore, it is difficult to obtain deposits with large grain size under constant current electrolysis. However, under pulsed current electrolysis, the slow mass transfer caused by diffusion seems to be modified. During current interruption stage, metal ions in the bulk electrolyte could transfer to the electrode surface by diffusion in order to maintain the large concentration in the vicinity of the electrode, to produce deposits with coarse particle size. Therefore, in NaCl-KCl-MnCl$_2$ (10 wt%) mixture, pulsed current electrolysis was performed to optimize the morphology of cathode product.

During the pulsed current electrolysis (current density: 0.3A·cm^{-2}), the periodic time (t) is selected as 10 min, different ratios of t_{on} to t_{off} (n=1, 2, 3) were attempted to establish optimum conditions for electrodeposition. The SEM images of produced manganese under these conditions are shown in fig. 4.
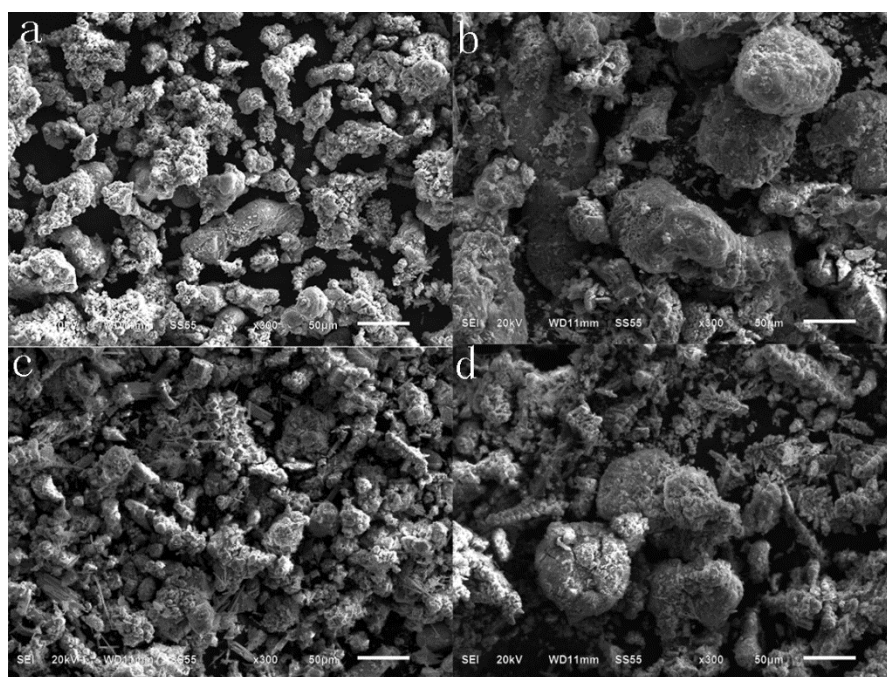

Figure 4. SEM images of the produced manganese at various ratios of t_{on} to t_{off} (n) in NaCl–KCl-MnCl$_2$ (10 wt%) melt at 983 K. Current density: 0.3A·cm^{-2}. （a）direct current;（b）n=1;（c）n=2;（d）n=3.

Fig. 4 (a) shows the morphology of manganese under constant current electrolysis and fig. 4 (b-d) show those under pulsed current electrolysis. Compared with fig. 4 (a), the particle size in fig 4 (b) becomes coarser. The particle size in fig. 4(c) and (d) exhibits no pronounced improvement. It is indicated that when t =10 min and n = 1, the morphology of produced manganese is obviously improved. Increasing the value of n to 2 or 3 results in no apparent enhancement. During the pulsed current electrolysis in the current interruption stage, the supplement of metal ions on the electrode surface could be achieved to maintain the stable concentration of metal ions, leading to coarsening of particle size. When n=1, interruption time is long enough for the replenishment of manganese ions, the morphology of manganese is effectively enhanced. On the other hand, when n=2 or 3, the interruption time may be short compared with the electrolysis time, so the replenishment of manganese ions could not be achieved. Therefore, no obvious enhancement of the morphology could be examined. Zhang et al. reported similar results in a study of pulsed current electrodeposition of titanium in molten salts [12].

3.2 Pulsed current electrolysis in NaCl-KCl-MnCl$_2$ with a high carbon ferromanganese anode

In molten NaCl-KCl-MnCl$_2$ (5 wt %) system at 983 K, high carbon ferromanganese was employed as the anode, a tungsten plate was used as the cathode, to produce ferromanganese. Galvanostatic electrolysis with a cathode current density of 0.3 A·cm^{-2} was implemented on the two-electrode cell, with the photo of cathode product and its XRD result shown in fig. 5.
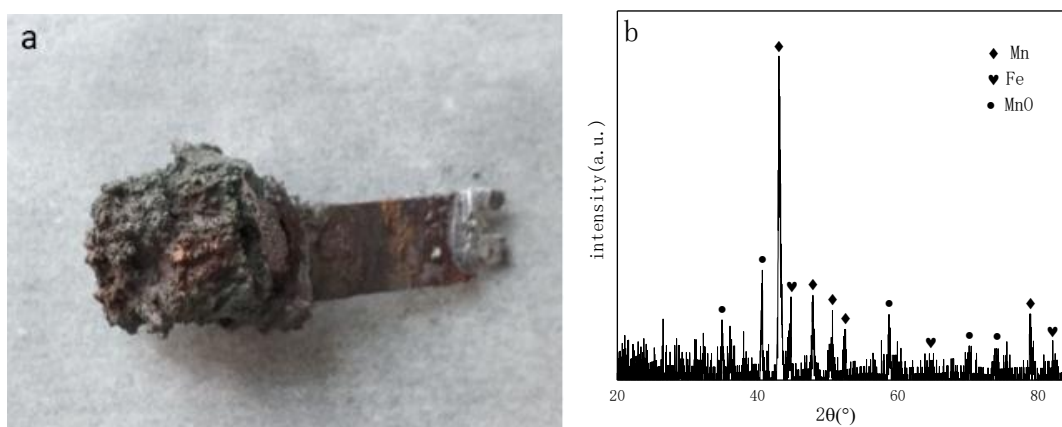

Figure 5. The photo of cathode deposit (a) and its XRD results (b) using high carbon ferromanganese as the anode under constant current electrolysis (0.3 A·cm^{-2}) in NaCl–KCl-MnCl$_2$ (5 wt%) melt at 983 K.

The cathode product was attached on the electrode surface. After washed in water and acetone, the product is powdery. From fig. 5 (b), the product mainly consists of manganese, and some iron. It also contains MnO, which could be due to the oxidation of manganese for contacting with water during its recovery process.

Subsequently, pulsed current was applied for the electrorefining of high carbon ferromanganese (n=1). In fig. 6 the SEM images of cathode product under constant current electrolysis (a) and pulsed current electrolysis (b, t=10min; c, t=20min) are demonstrated.
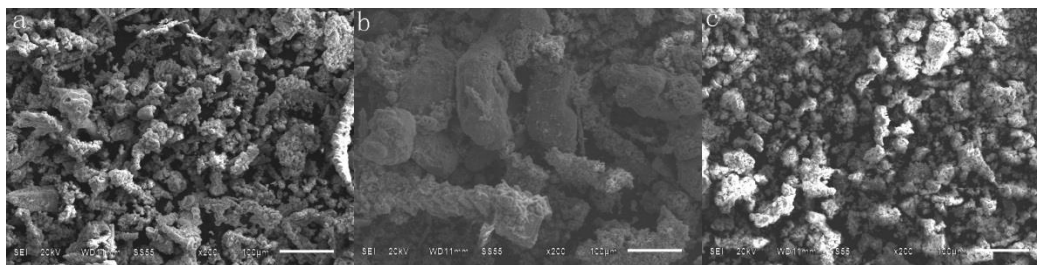
Figure 6. SEM images of produced manganese and iron with various periodic time (t) in NaCl–KCl-MnCl$_2$ (5 wt%) melt at 983 K (n=1). (a) direct current; (b) t=10min; (c) t=20min.

As seen from fig. 6, it is found that compared with fig. 6 (a), the particle size in (b) becomes coarser, but the particle size in (c) is close to that in (a). When t=20 min, the current interruption time is relatively short for the replenishment of consumed metal ions in the vicinity of electrode, as indicated in section 3.1. In this case, the periodic time set as 10 min is better during the pulsed current electrorefining of high carbon ferromanganese.

From the above results, it is found that pulsed current electrolysis could improve the quality of cathode product. It is important to select the pulsed parameters, especially the periodic time and the ratio of t_{on} to t_{off}. The duration of t_{off} should be long enough for the replenishment of consumed metal ions by diffusion to weaken concentration polarization [11-12].

4. CONCLUSIONS

Pulsed current electrolysis were employed in NaCl-KCl-MnCl$_2$ (10 wt %) melt at 983K. A tungsten wire was used as the cathode and a carbon rod was used as the anode. Under a cathode current density of 0.3 A·cm^{-2}, the periodic time was selected as 10 min and different ratios of t_{on} to t_{off} were applied. Comparing with that under direct current, the particle size of produced manganese (t=10 min; n=1) becomes coarser obviously. It indicates that the adoption of pulsed current electrolysis could improve the morphology of cathode product. When the value of n increased to be 2 or 3, the effect of pulsed current electrolysis is decreased, which suggests that a suitable value of n is of significance. In addition, high carbon ferromanganese was used as the anode, and a tungsten plate was used as the cathode. It is also found that the morphology of produced manganese and iron under pulsed current electrolysis (t=10 min; n= 1) becomes better with bigger particle size. Therefore, under the employment of pulsed current electrolysis with proper parameters, the improvement of the morphology of the cathode product could be achieved.

References

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