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The Electrochemical Behavior of Cr(II) Ions in NaCl-KCl Melt

Wei Liu[1, 2], *Guolong Liu*[1, 2], *Saijun Xiao*[1, 2*], *Jun Zhang*[1, 2]

[1]School of Metallurgy Engineering, Anhui University of Technology, Maanshan 243000, China
[2] Key Laboratory of Metallurgical Emission Reduction & Resources Recycling, Ministry of Education, Anhui University of Technology, Maanshan, Anhui, 243002, China
[*]E-mail: xiaosaijunzj@yahoo.com

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The cathodic behavior of Cr (II) ions on Pt electrode in molten NaCl-KCl mixture at a temperature of 710 ℃ (983K) was investigated by cyclic voltammetry, square wave voltammetry, chronopotentiometry, and chronoamperometry. The results indicate the reduction process of Cr (II) to Cr on Pt electrode was one step: $Cr^{2+}+2e^{-}=Cr$. Reduction of Cr (II) ions is a quasi-reversible process controlled by diffusion mass transfer, and the reduction product is insoluble. The diffusion coefficient for chromium (II) ions in NaCl-KCl melt calculated by the data of cyclic voltammetry and chronopotentiometry, is 1.31×10^{-5} $cm^2\cdot s^{-1}$ and 1.15×10^{-5} $cm^2\cdot s^{-1}$, respectively. The growth process of Cr (II) ions on Pt electrode was instantaneous three-dimensional nucleation. Potentiostatic electrolysis performed on the Pt electrode confirmed the feasibility of electrodepositing metallic chromium in the molten NaCl-KCl-$CrCl_2$ system.

Keywords: molten salt; chromium; electrochemical behavior; diffusion coefficient; potentiostatic electrolysis

1. INTRODUCTION

Chromium and its alloy have been widely used in metallurgy, chemical industry, automobile manufacturing and aerospace industry for their desirable properties such as high boiling point, high melting point, high strength, excellent corrosion resistance and good ductility [1-3]. Thermal reduction and electrolytic process are usually used to prepare chromium metal. However, the produced chromium by thermal reduction is usually contaminated by other metals such as Al and Si. The thermodynamic and kinetic data related to chromium plating also indicates that it is very difficult to obtain the electrodeposition of chromium from aqueous solutions without hydrogen production [4]. Moreover, the chromium electroplating process produces vast polluting wastes with significant amounts of chromium (VI) species. Compared with thermal reduction and aqueous solution electrolysis process, molten salt technology has received more attention owing to its unique advantages, such as the high electrical conductivity, high current density, environmentally friendly characteristics. Weng et al. [5] have reported that metallic chromium can be directly obtained from K_2CrO_4 in the $CaCl_2$-KCl molten salt. Hyslop and his co-workers [6], in their study of utilization of constant current chrononpotentiometry to synthesize a Co-Cr alloy, indicated that the Co-30 wt % Cr alloy was prepared successfully via electro-deoxidation in molten calcium chloride. Chen et al. [7, 8] investigated the direct electrochemical reduction of Cr_2O_3 in $CaCl_2$ melt and got the pure metal chromium. In addition, there are many studies about the preparation of metallic chromium by molten salt electrolysis which were reported [9-12]. In 1969, chromium was obtained from high-carbon ferrochromium by molten salts electrorefining in different melts, but still with some impurities in the produced chromium [13]. This is a promising method due to the low cost of the starting material, and the selection of NaCl-KCl system could be more attractive due to its convenience to be processed. Therefore, it is necessary to investigate the cathodic behavior of chromium ions in NaCl-KCl melt.

Many researchers have studied the electrochemical behavior of chromium ions in molten salt [14-20]. It was found that in the eutectic LiCl-KCl molten salt nucleation phenomena of metallic chromium was shown obviously, especially glass carbon as working electrode [15]. Cotarta et al. [16, 17] used different kinds of electrochemical techniques to investigate the cathodic behavior of Cr (III) ions in the LiCl-KCl eutectic melt, and concluded that the reduction process of Cr (III) ions in this system is a two-step process: $Cr^{3+}+e^{-}=Cr^{2+}$ and $Cr^{2+}+2e^{-}=Cr$. Vargas et al. [18] studied the relationship between the electrochemical parameters and the resulting structures of chromium electrodeposits in the LiCl-KCl eutectic melt, which demonstrates that electrocrystallization may be controlled by using different potential functions. Duan et al. [19] found that the Cr (II) species were reduced to the metal through a single step with two electrons exchanged, and reduction of Cr (II) ions is quasi-reversible, which is controlled by diffusion mass transfer in the LiCl-KCl eutectic melt. Nevertheless, the electrochemical data of Cr (II) ions in molten NaCl-KCl have not been investigated intensively.

This paper focused on the cathodic behavior of Cr (II) ions in molten NaCl-KCl mixture to achieve reduction parameter of chromium ions and the mechanism of electrodeposition of chromium to provide theoretical guidance for subsequent study of electrorefining of high-carbon ferrochromium to prepare pure chromium in this system.

2. EXPERIMENTAL

2.1 Experimental apparatus

The whole apparatus which was used for electrochemical test was illustrated in Fig.1. All electrochemical tests were conducted with a three-electrode electrochemical cell. A platinum wire (Tianjin Lucheng Metal Manufacturing Co., Ltd., 99.95%) with a diameter of 1 mm was employed as the working electrode (WE). The counter electrode (CE) was a spectroscopically pure graphite rod (Zibo Jinpeng Carbon Co., Ltd., 99.99%) with a diameter of 8 mm. An Ag/AgCl electrode being the reference electrode (RE) was prepared by putting a silver wire with a diameter of 1mm in a mullite tube containing silver chloride solution in NaCl-KCl molten mixture. The electrodes were polished with sand paper, and then rinsed with ethanol prior to each measurement.

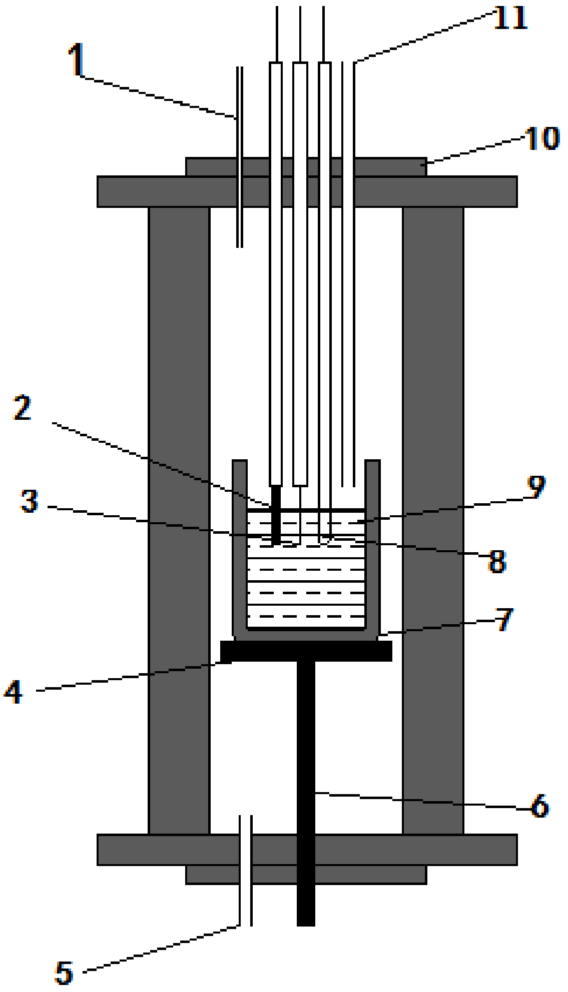

Figure 1. Experimental set-up for electrochemical measurements. 1-tube for argon in, 2-counter electrode, 3-working electrode, 4-graphite supporter, 5-tube for argon out, 6-stainless steel bar, 7-aluminium oxide crucible, 8-reference electrode, 9-molten salt, 10-cooling system, 11-tube for adding $CrCl_2$

2.2 Preparation of the molten salt

Reagents of the experiments were NaCl (Sinopharm Chemical Reagent Co., Ltd.), KCl (Sinopharm Chemical Reagent Co., Ltd.), and $CrCl_2$ (Sinopharm Chemical Reagent Co., Ltd.), all of which were analytical reagent. The mixture of NaCl-KCl molten salt (50.6:49.4 mol %) which was used as electrolyte was firstly dried under vacuum for more than 48 h at 200 °C (473 K) to remove surface water. Then the mixture was transferred to an alumina crucible container. The crucible was moved into the furnace and heated under argon atmosphere by elevating temperature to 200°C (473 K) for 2 h and then to the working temperature of 710°C (983 K).

2.3 Electrochemical measurements

The electrochemical properties of Cr (II) ions was investigated by means of cyclic voltammetry, square wave voltammetry, chronopotentiometry, and chronoamperometry which were equipped by a powersuite software in a computer connected with an electrochemical workstation (Model PARSTAT2273) (Princeton Applied Research, AMETEK). All the electrochemical tests were carried out under dry argon atmosphere with the working temperature of 710°C (983 K) to prevent unnecessary oxidation reactions. The Pt electrode (WE) was immersed into NaCl-KCl melt about 10 mm.

2.4 Production of chromium deposit

In order to assess the feasibility of chromium electrodeposition in the electrolyte of NaCl-KCl-$CrCl_2$, the deposition of chromium was carried out in NaCl-KCl melt containing $CrCl_2$ at 710°C (983 K). After the electrolysis, the obtained products which have been washed with water and acetone, and also been dried in vacuum drying oven were characterized by scanning electron microscope (SEM) (JSM-6510LV; JEOL), and X-ray diffraction (XRD) (Bruker D8 Advance; Bruker corporation, Germany).

3. RESULTS AND DISCUSSION

3.1 Cyclic voltammetry

Fig. 2 presents the cyclic voltammograms recorded on platinum electrode at different scan rates (from $0.1 V\cdot s^{-1}$ to $0.8 V\cdot s^{-1}$) in NaCl-KCl-$CrCl_2$ ($C=3.33\times10^{-4} mol\cdot cm^{-3}$) molten system at 710°C (983 K). It exhibits one pair of peaks (A1 and A2) in Fig. 2. The reduction peak A1 corresponds to the reaction of Cr (II) to Cr, and the oxidation peak A2 is attributed to the dissolution of chromium, which indicates that chromium ion could be deposited in a single step: $Cr^{2+}+2e^{-}=Cr$. The reduction of Cr (II) ions starts from around -0.73 V (vs Ag/AgCl) in this system. Furthermore, the peak potential shifts slowly to the negative side with the increasing of the scan rate, which demonstrates the reduction process from chromium (II) to chromium metal is a quasi-reversible reaction.

In order to obtain the diffusion coefficient of the chromium (II) ions, the relationship between cathodic peak current density and square root of the scan rate was given in Fig. 3. The cathodic peak current density (I_p) varies linearly with square root of the scan rate ($v^{1/2}$), which obey the Randle-Sevick equation. It indicates that the reduction of Cr (II) on platinum electrode was controlled by diffusion step. Based on the slope value of the straight line in Fig. 3 and Equation (1) [21], the diffusion coefficient of Cr (II) ion is calculated as $1.31\times10^{-5} cm^2 s^{-1}$.

$$I_p=-0.61nFSC^0(nF/RT)^{1/2}D^{1/2}v^{1/2} \qquad (1)$$

where n is the number of exchanged electrons, F the Faraday constant (96485C·mol^{-1}), S the electroactive area (cm^2), C_0 the concentration of Cr (II) ions (mol·cm^{-3}), T the temperature (K), D the diffusion coefficient (cm^2·s^{-1}), and v the scan rate(V·s^{-1}).

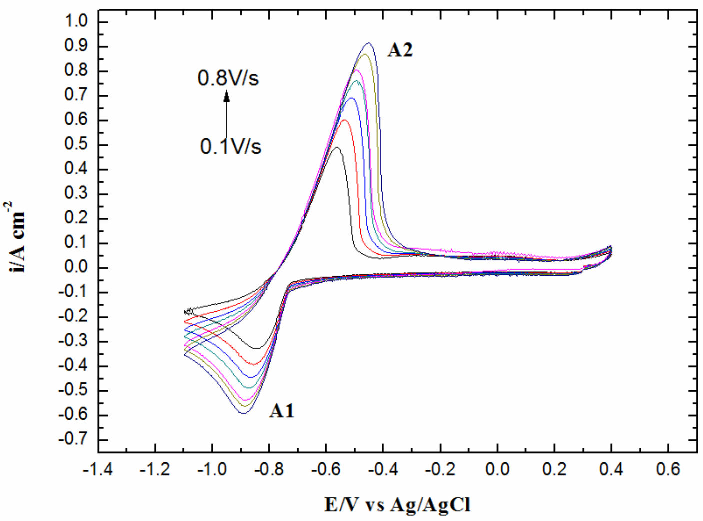

Figure 2. Cyclic voltammograms on platinum electrode at different scan rates in NaCl-KCl-$CrCl_2$ (C=3.33×10^{-4} mol·cm^{-3}) melt at 710°C (983 K).

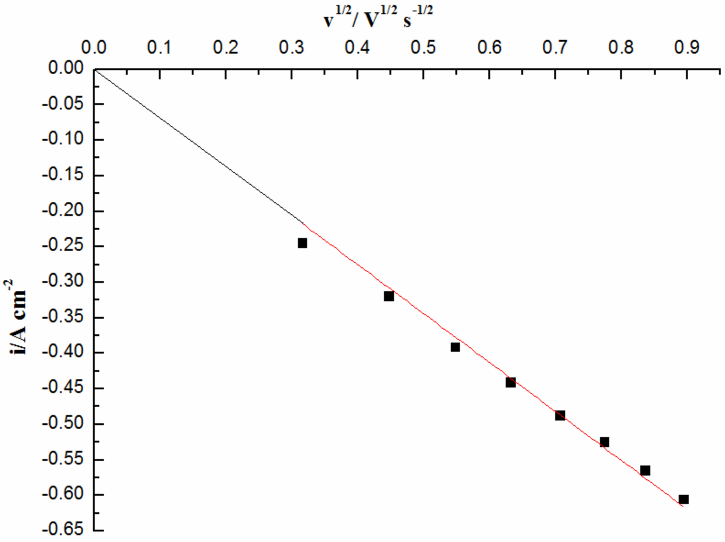

Figure 3. The liner relationship of cathodic peak current density (I_p) vs. square root of scan rate ($v^{1/2}$).

3.2 Square wave voltammetry

In order to further study the cathodic behavior of Cr (II) ions in the NaCl-KCl-$CrCl_2$ (C=3.33×10^{-4}mol·cm^{-3}) melt, square wave voltammetry was performed on platinum electrode, and the corresponding result was presented in Fig. 4. It is observed that there is only one peak during negatively potential sweeping. It was found that the single peak is not symmetric which is not consistent with the prediction by theory, which results from the nucleation effect. The formation of solid phase resulted in the appearance of the nucleation overpotential which directly hindered the increase of current. It would be a good method that the decreasing part of the peak for measurements of the half width in Fig. 4 is only considered to resolve the disturbance of the signal caused by the nucleation.

According to the half width in Fig. 4 and Equation (2) [22], the number of exchanged electrons could be computed, and the result is close to 2 (2.1). A conclusion can be reached that there are two electrons exchanged during the reduction process of Cr (II) to Cr, which is consistent with the hypothesis obtained from cyclic voltammetry.

$$W_{1/2}=3.52RT/nF \qquad (2)$$

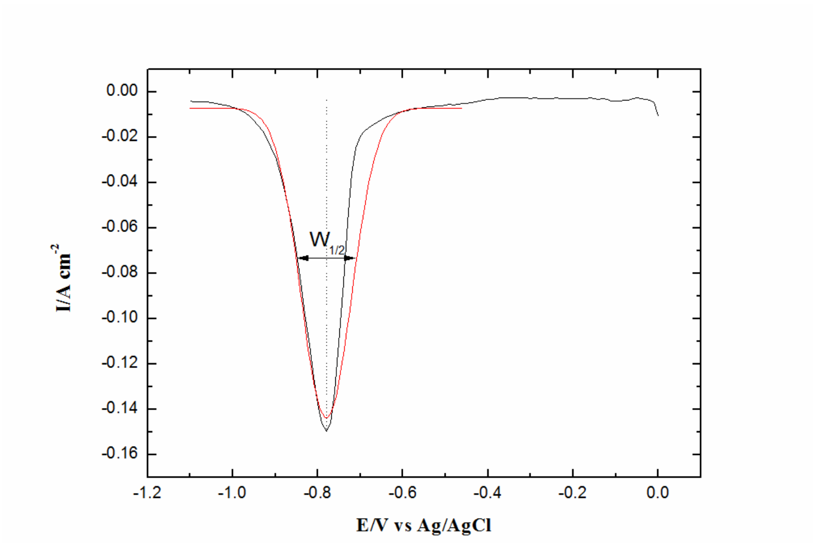

Figure 4. Squre wave voltammogram on platinum electrode in NaCl-KCl-$CrCl_2$ ($C=3.33\times10^{-4}mol\cdot cm^{-3}$) melt at 710°C(983K).

3.3 Chronopotentiometry

To confirm the validity of the above results, chronopotentiometry was used to investigate the cathodic process of Cr (II) ions on platinum electrode in the NaCl-KCl-$CrCl_2$（$C=2.16\times10^{-4}mol\cdot cm^{-3}$）melt at 710°C (983 K), and the result was given in Fig. 5. There are two potential platforms which can be clearly observed. The former potential platform of -0.8 V (vs Ag/AgCl) is associated with the reduction process of Cr (II) ions to chromium metal, which is close to the value of cyclic voltammetry.

It was shown in Fig. 6 that he value of $I\tau^{1/2}$ is almost constant with the change of the applied current. Therefore, the electrochemical reduction process was regarded as a process controlled by the diffusion of Cr (II) ions, which is the same as the conclusion drawn in cyclic voltammetry.

Fig. 7 shows the liner relationship between E and $ln[(\tau^{1/2}-t^{1/2})/\tau^{1/2}]$. It is obvious that there is a good liner relationship, indicating the electrochemical process is reversible, and deposited products were insoluble. In addition, based on the slope value of the straight line in Fig. 7 and the Equation (3) [23], the number of exchanged electrons (n) was calculated, which is also close to 2 (1.9). It further proved the one-step process taking place during the reduction of Cr (II), which accords with the result calculated by square wave voltammetry.

$$E=E_{\tau/4}+(RT/nF)\ln[(\tau^{1/2}-t^{1/2})/\tau^{1/2}] \quad (3)$$

Where τ is the transition time (s), t the polarization time (s), n the exchanged electrons number, F the Faraday constant (96485C·mol^{-1}), T the temperature (K).

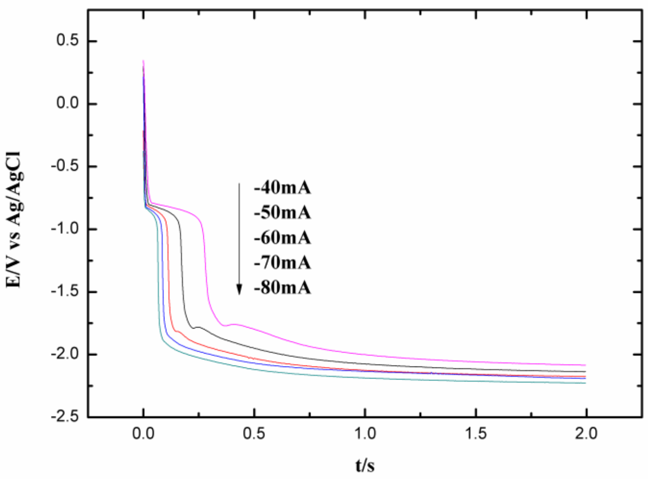

Figure 5. Chronopotentiograms on platinum electrode with applied various currents in NaCl-KCl-$CrCl_2$ (C=2.16×10^{-4} mol·cm^{-3}) melt at 710°C (983 K).

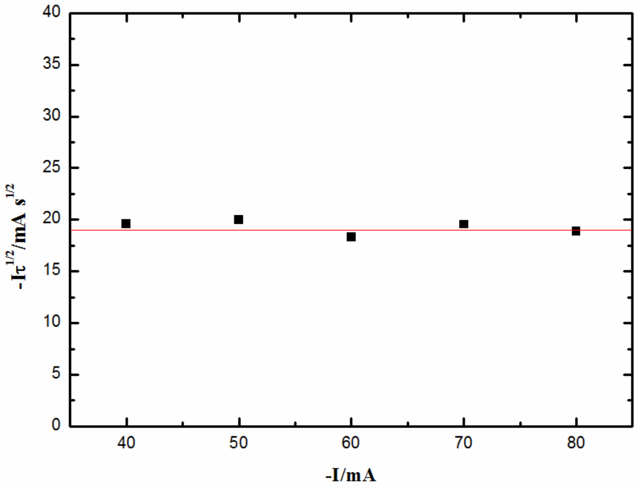

Figure 6. The relationship between I and $I\tau^{1/2}$ in NaCl-KCl-$CrCl_2$ (C=2.16×10^{-4} mol·cm^{-3}) melt at 710°C (983 K).

Since the reduction process of chromium (II) on platinum electrode was a diffusion-controlled process, the diffusion coefficient can be also computed by the Sand's law (4) [24]:

$I\times\tau^{1/2}=0.5nFSC^0(\pi D)^{1/2}$ (4)

Where I is applied the current (A), τ the transition time (t), n the exchanged electrons number, F the Faraday constant ($96485C\cdot mol^{-1}$), S the electroactive area (cm^2), C_0 the concentration of Cr (II) ions ($mol\cdot cm^{-3}$) and D the diffusion coefficient ($cm^2\cdot s^{-1}$).

The transition time τ was measured from Fig. 5 when the applied current is -50 mA and *D* is calculated as 1.15×10^{-5} $cm^2\cdot s^{-1}$, which agrees with the value by calculation from previous cyclic voltammograms.

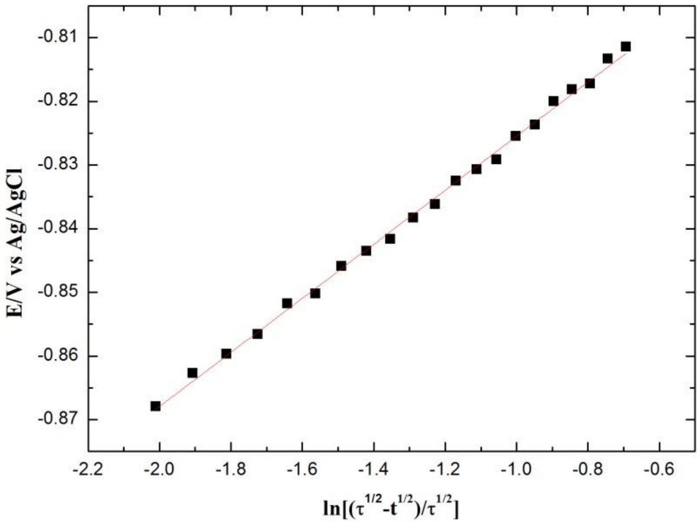

Figure 7. The liner relationship between *E* and $ln[(\tau^{1/2}-t^{1/2})/\tau^{1/2}]$ in NaCl-KCl-$CrCl_2$ ($C=2.16\times10^{-4}$ $mol\cdot cm^{-3}$) melt at 710°C (983 K).

3.4. Chronoamperometry

Based on the data of cyclic voltammetry, square wave voltammetry and chrononpotentiometry, chrononamperometry was used to investigate the nucleation process of chromium on platinum electrode. A series of current-time curves were obtained at different applied constant potential, which were recorded in Fig. 8. Firstly, the current rise to a certain value from zero under constant potential; then the current decreased rapidly with time which is attributed to the charge process of the electrode electric double layer and the incubation stage of the crystal nucleus; with the formation of a new phase, the crystal nucleus continued to grow while the actual cathode area increased; eventually, the current became to be stable gradually.

In the document [25], two kinds of nucleation processes are introduced: instantaneous nucleation and processive nucleation which are represented by Equation (5) and (6) respectively:

$I(t)=[nFN_0\pi(2DC)^{3/2}M^{1/2}/\rho^{1/2}]\times t^{1/2}$ （5）

$I(t)=[2nFK_nN_0\pi(2DC)^{3/2}M^{1/2}/3\rho^{1/2}]\times t^{3/2}$ （6）

Where N_0 is the initial nucleation number, n the exchanged electrons number, M the atomic weight for deposits ($g \cdot mol^{-1}$), D the diffusion coefficient ($cm^2 \cdot s^{-1}$), C the concentration of Cr (II) ($mol \cdot cm^{-3}$), ρ the density for deposits ($g \cdot cm^{-3}$), I(t) the polarization current (A), and K_n the nucleation constant.

Typical plots of *I* against $t^{1/2}$ are shown in Fig. 9 for different overpotentials, suggesting that the initial periods of electrochemical deposition of chromium ions on platinum electrode can be seen as a model involving instantaneous three-dimensional nucleation.

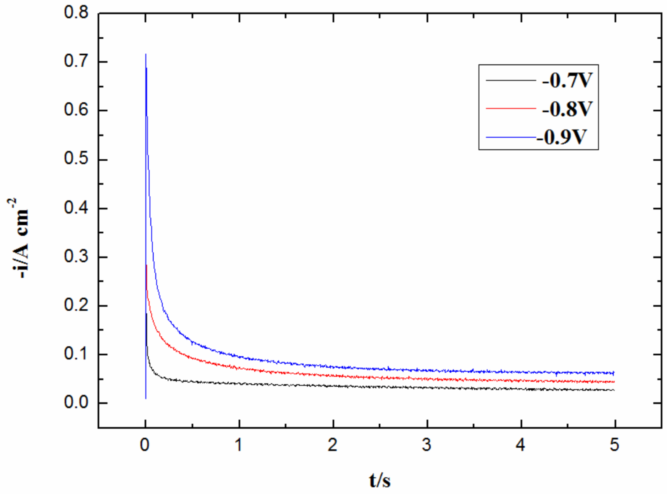

Figure 8. Chronoamperograms on platinum electrode in NaCl-KCl-$CrCl_2$ ($C=2.16\times10^{-4} mol \cdot cm^{-3}$) salt at 710°C (983 K).

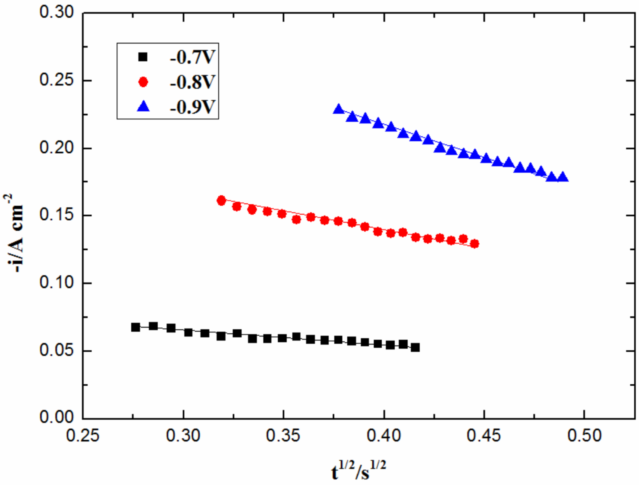

Figure 9. The relationship between *I* and $t^{1/2}$ in NaCl-KCl-$CrCl_2$ ($C=2.16\times10^{-4}$ $mol \cdot cm^{-3}$) melt at 710°C (983 K).

3.5 Electrolysis

After the electrochemical tests, the electrodeposition was carried out with constant potential (-1.1V vs Ag/AgCl) in an electrolyte of NaCl-KCl-$CrCl_2$ ($C=2.16\times10^{-4}$ $mol \cdot cm^{-3}$) melt. The photograph of electrolytic chromium was shown in Fig. 10(a), which is fine powder with green appearance, due to the formation of Cr_2O_3 by oxidation of the surface layer. The SEM image of deposited Cr was shown in Fig. 10(b). It is observed that there are different sizes of chromium particles, which could be due to different current density during the electrolysis process. The bigger size could be around 50 um. Fig. 11 is the XRD pattern of electrolytic products, which confirmed the electrolytic product was chromium metal with minor Cr_2O_3 shown in Fig. 10(a). The existence of Cr_2O_3 is probably due to the contact with water and air during the process of product after the electrolysis.

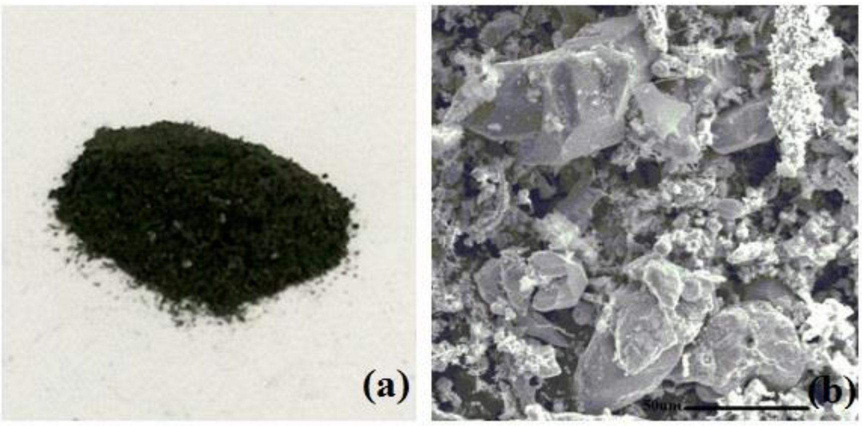

Figure 10. (a) the photograph of the chromium deposited.(b) SEM image of electrolytic Cr.

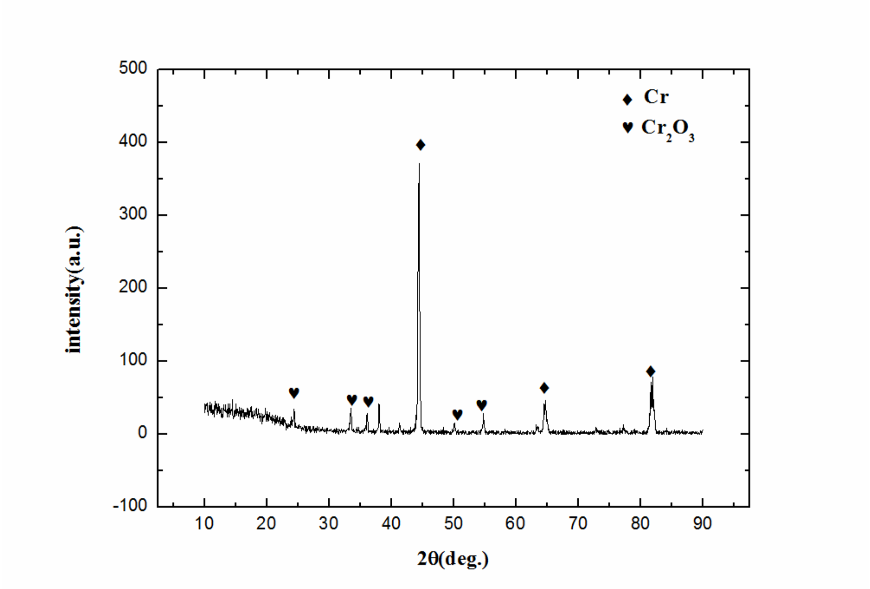

Figure 11. The XRD pattern of electrolytic products on a platinum electrode in NaCl-KCl-$CrCl_2$ (C=3.33×10^{-4} mol·cm^{-3}) melt.

4. CONCLUSIONS

The cathodic behavior of Cr (II) ions in NaCl-KCl salt at the temperature of 710°C(983K) was studied on platinum electrode. The results indicate that the cathodic reduction of chromium ion was a one-step and quasi-reversible reaction controlled by diffusion, and the reduction product was insoluble. The diffusion coefficient for the Cr (II) ions in the NaCl-KCl system calculated by cyclic voltammetry was almost equal to that computed by chronopotentiometry, which is 1.31×10^{-5} $cm^2\cdot s^{-1}$ and 1.15×10^{-5} $cm^2\cdot s^{-1}$, respectively. The mechanism of nucleation of Cr electrodeposition was three-dimensional instantaneous nucleation. It is feasible to achieve the electrodeposition of Cr under constant potential in molten NaCl-KCl-$CrCl_2$ system.

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