

Investigation on the Oxidation and Reduction of Titanium in Molten Salt with the Soluble TiC Anode



SHULAN WANG, CHAOPIN WAN, XUAN LIU, and LI LI

To reveal the oxidation process of titanium from TiC anode and the reduction mechanism of titanium ions in molten NaCl-KCl, the polarization curve of TiC anode in molten NaCl-KCl and cyclic voltammograms of the molten salt after polarization were studied. Investigation on the polarization curve shows that titanium can be oxidized and dissociated from the TiC anode at very low potential. The cyclic voltammograms demonstrated that the reduction reaction of titanium ions in the molten salt is a one-step process. By potentiostatic electrolysis, dendritic titanium is obtained on the steel plate. The work promotes the understanding on the process of electrochemical oxidation/dissociation of titanium from TiC anode and the reduction mechanism of titanium ions in molten salt.

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TITANIUM and its alloys have wide applications in microelectronics, biomaterials, and aerospace because of their excellent physicochemical properties, such as high strength, low density, high temperature stability, and excellent corrosion resistance.^[1-3] Tremendous efforts have been made in the past two decades to establish new processing routes to replace the existing Kroll process,^[4] which has the disadvantages of high economic input. The novel FFC Cambridge process has been proposed to extract titanium from titanium dioxide,^[5-7] and has been extended to extract a wide range of active metals and alloys.^[8-14] The FFC Cambridge process has also been used to prepare Ti₂CO_n functional materials for the application of surface decoration.^[15] Other titanium extraction methods have also been developed, such as the Ono Suzuki process which combines calcium thermal reduction and an electrolysis process in the same cell,^[16,17] the direct molten oxide electrolysis at temperatures above the melting point of mixed oxide,^[18] and the USTB process^[19,20] in which Ti₂CO as the soluble anode is electrolyzed in the molten salt. In addition, Takeuchi *et al.* conducted potentiostatic electrolysis in molten NaCl-KCl-TiCl₂-TiCl₃ using TiC, TiO, and Ti-C-O as anodes.^[21,22] In the case of TiC anode, titanium was extracted at high ratio with low carbon content due to carbon produced *in situ* in the TiC anode. However, the fundamental investigation of anode dissociation/titanium deposition was not performed and the redox reaction mechanism of the electrolysis is still unknown.

Understanding the diffusion and reaction behaviors of the active species in electrolytes is very important for achieving high efficiency of electrolysis and revealing corresponding reaction mechanisms of the electrodes.^[23-26] For example, the diffusion coefficient of metallic ion Zn²⁺, Pb²⁺, and Mg²⁺ in molten KCl-LiCl has been studied and compared with the result obtained from various electrochemical techniques.^[23] The electrochemical behavior of Fe³⁺ in CaCl₂-KF has also been studied by cyclic voltammetry/chronopotentiometry and the electrochemical kinetics has been analyzed.^[24] Among all molten salt systems, the NaCl-KCl mixture has several advantages over the others, such as a high electrical conductivity, a low melting point, absence of moisture absorbance, and low cost.^[27] Furthermore, the NaCl-KCl mixture has the second widest potential window due to the high decomposition potentials of 3.18 and 3.45 V at 1073 K (800 °C), respectively, for NaCl and KCl.^[28] TiC has the electrical conductivity as high as $4.75 \times 10^5 \text{ S m}^{-1}$ even at room temperature^[29] and is considered as one of the best soluble anode candidates.

In the present work, polarization curve of TiC anode and cyclic voltammograms of molten NaCl-KCl and potentiostatic electrolysis were investigated and performed aiming to enhance the understanding on the process of electrochemical oxidation as well as dissociation of titanium from TiC anode and the reduction mechanism of titanium ions in molten salt by using techniques such as linear sweep voltammetry and cyclic voltammetry. The current study provides the important scientific guidance for the further improvements of titanium processing by molten salt electrolysis.

TiC powder (99 pct, Institute of Non-ferrous Metal, Beijing) and polyethylene glycol (~1 wt pct used as binder) were mixed and pressed into pellets (15 mm in diameter and 3 mm in thickness). The pellets were then sintered in argon atmosphere at 1223 K (950 °C) for 4 hours with a heating rate of 5 °C min^{-1} and a hole was drilled in the upper side of each pellet. A thin nickel

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wire (0.2 mm in diameter) was used to hold the pellets to a molybdenum wire (1.5 mm in diameter) as the anode. NaCl and KCl (A.R., Sinopharm Chemical Reagent Co., Ltd, China) in equal molar ratio were mixed manually and dried at 473 K (200 °C) for 48 hours. The mixture was then placed into an alumina crucible (42 mm in inner diameter, 800 mm in height) in a vertical furnace as the electrolyte. The furnace was filled with flowing argon (99.99 pct) for 10 hours before heating.

Both polarization curves of the TiC anode and the graphite anode were measured in equimolar KCl-NaCl by linear sweep voltammetry. The cyclic voltammograms of the molten salts after polarization were investigated with molybdenum wire as the working electrode. The Ag/AgCl reference electrode was prepared by dipping Ag wire (1.5 mm in diameter) into a pre-dried 45 pct NaCl-45 pct KCl-10 pct AgCl (mol pct) mixture, which was held in an alumina tube with a slot and then heated to melt.^[30] Potentiostatic electrolysis was performed for the production of titanium in molten NaCl-KCl with the one-time addition of 1 mol pct TiCl₂ (99.98 pct, anhydrous, Sigma-Aldrich) at the potential of -1.3 V between the cathode and anode. In the two-electrode cell, a steel plate (square in shape and 4 cm² in area) served as the cathode electrode and TiC served as the anode. All experiments were performed at 1073 K (800 °C) for achieving the excellent fluidity for NaCl-KCl melt under Ar atmosphere. The purpose of TiCl₂ addition is to achieve a stable initial electrolysis current in the molten salt. The corresponding electrochemical measurement was conducted by Potentiostat/galvanostat model 273A & Lock amplifier 5210. All electrodes were lifted out of the molten salt and naturally cooled in the furnace in an argon atmosphere after measurement. The detailed experimental setup is shown in Figure 1(a). The cathode deposit was washed by water and diluted HCl (0.05 M), and dried naturally for further structural characterization. X-ray diffraction patterns were collected to analyze the phase composition of the product with a Philips PW3040/60 diffractometer (CuK α source, $\lambda = 0.15406$ nm) at the rate of 0.03 deg min⁻¹ in the 2 θ range of 30 to 90 deg. Scanning electron microscope (Shimadzu, SSX-550), operated at an acceleration voltage of 30 kV, was used to analyze the surface morphology of the deposit.

The polarization curve of TiC anode in the potential range between 0 and 2.0 V at 1073 K (800 °C) was studied by linear sweep voltammetry at the low sweep rate of 10 mV s⁻¹ to investigate the electrochemical oxidation and dissociation of titanium from TiC anode and is shown in Figure 1(b). TiC lost electrons at the applied potential and dissolves in the molten salt in the form of titanium ions, which then moved to the cathode and were reduced there. Potential scan at the low rate led to oxidizing enough titanium and guaranteed apparent reduction/oxidation current peaks on subsequent cyclic voltammograms. In the current work, graphite was used to further study the electrochemical properties of the molten salt. The corresponding polarization curve is also presented in Figure 1(b). It can be observed that the current in the polarization curve of TiC anode shows

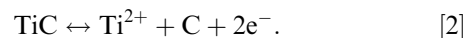
a dramatic linear increase from 0.7 V with the increase in potential, which should correspond to the oxidation and dissociation of titanium from TiC anode because titanium can be electrochemically oxidized and dissociated from TiC anode before the decomposition of NaCl and KCl due to the low decomposition potential of TiC (0.89 V at 1073 K (800 °C)^[28]) and its lower thermodynamic stability than NaCl and KCl. The linear increase of the polarization current of TiC anode with an increasing potential also confirms that the oxidation and dissociation process of titanium from TiC is the rate-limited step. In the polarization curve of the graphite anode, the current is increased with the increase of potential from a high potential (1.4 V) corresponding to the evolution of chlorine on graphite anode.

In Figure 2, cyclic voltammograms of the molten salts on the molybdenum electrode were investigated in the potential range of 0 to -2.5 V after the polarization experiments of both the TiC anode and the graphite anode. The sharp peak started from the potential of -2.0 V in the cyclic voltammograms of the molten salt after polarization of the graphite anode is attributed to reduction of Na⁺ and K⁺ in the molten salt. The corresponding oxidation current peak in the reverse scan appeared at the potential of -1.75 V. No other reduction/oxidation current peak is observed in the cyclic voltammograms. The cyclic voltammograms of the molten salt after TiC anode polarization showed a couple of reduction/oxidation current peaks at the potential of -0.5 to -0.7 V, which are ascribed to the oxidation/reduction of Ti ions in the molten salt. This result is consistent with the results of the polarization curve and the thermodynamic analysis that Na⁺ and K⁺ in the molten salt have higher negative reduction potential than Ti ions. Investigation of cyclic voltammograms confirms that titanium is oxidized and dissociated from the soluble TiC anode in molten NaCl-KCl.

In addition, the results shown above further revealed that the reduction process of Ti ions in the molten salt to metallic Ti is a reversible one-step reaction and no other Ti ions in different valences were involved in the process. The following equation is used to determine the electron transfer number of Ti ions during the reduction process:^[31]

$$E_{p/2} = E_{1/2} + 28/n. \quad [1]$$

In Eq. [1], $E_{p/2}$ (mV) is the half peak potential, $E_{1/2}$ (mV) the average value of potentials E_p (the peak potential in the cyclic voltammograms) and $E_{p/2}$, and n is the electron transfer number. According to Eq. [1], Ti²⁺ was produced in molten NaCl-KCl during polarization of the TiC anode:



The titanium deposition experiment was conducted in molten NaCl-KCl-1 mol pct TiCl₂ for 10 h at a constant potential of -1.3 V in a two-electrode cell with TiC as the anode and a steel plate as the cathode. The potential of 1.3 V over the cathodic peak potential of 0.9 V in the

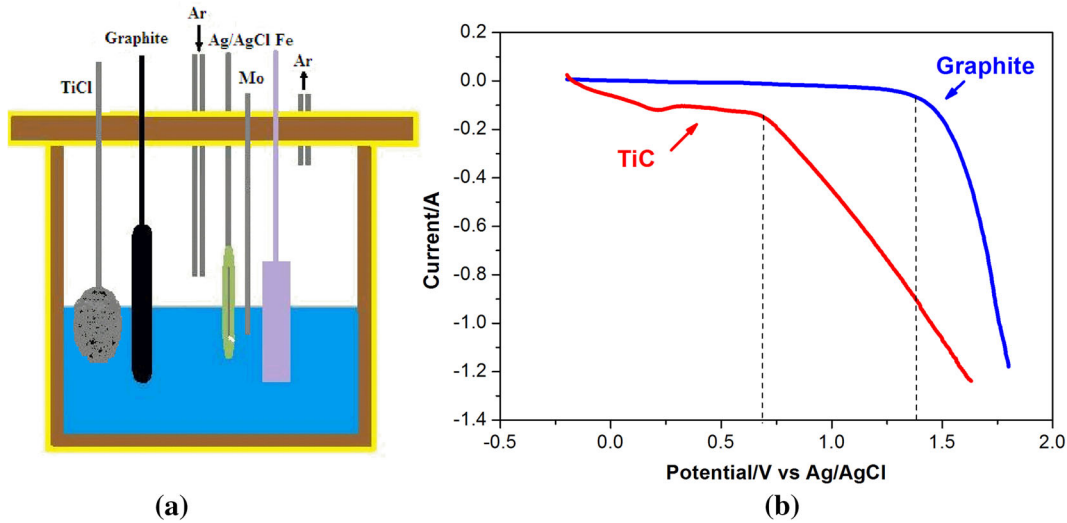


Fig. 1—(a) Experimental setup for the electrochemical characterization of molten salt; and (b) polarization curves of graphite and TiC anode in molten KCl-NaCl at 1073 K (800 °C).

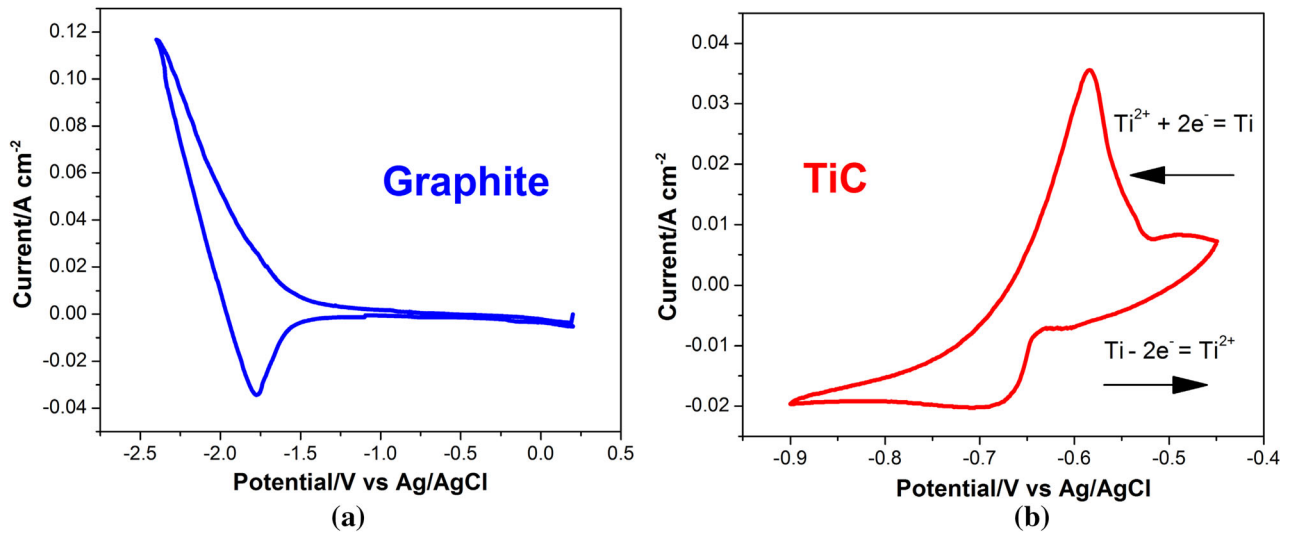


Fig. 2—Cyclic voltammograms of the molten salts after polarization with the (a) graphite and (b) TiC anode.

cyclic voltammogram (Figure 2(b)) was applied for achieving a high electrolysis rate. The initial Ti^{2+} concentration in the molten salt is necessary for achieving an apparent stable current during the electrolysis process. Since the theoretical decomposition potentials of NaCl and KCl are higher than 3.0 V, no faradic current will be formed for the electrolysis in molten NaCl-KCl at the potential of 1.3 V. Titanium ion is dissociated from TiC anode by capturing electrons during the electrolytic process, while the initial current during the electrolyte process is required before the titanium ion moves and arrives at cathode. With the one-time addition of 1 mol pct $TiCl_2$ in the molten salt, the reduction of $TiCl_2$ to Ti metal on the cathode can maintain the initial electrolyte current. Figure 3 shows the time courses of current and potential for titanium electrolysis from molten NaCl-KCl-1 mol pct $TiCl_2$ at

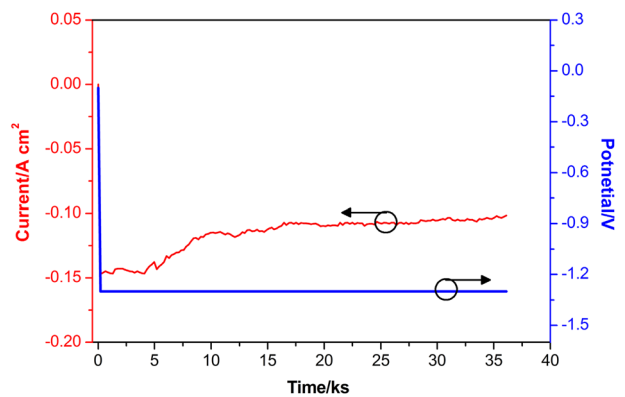


Fig. 3—The electrodeposition curve of titanium from molten NaCl-KCl-1 mol pct $TiCl_2$ at 1073 K (800 °C) using the soluble TiC anode.

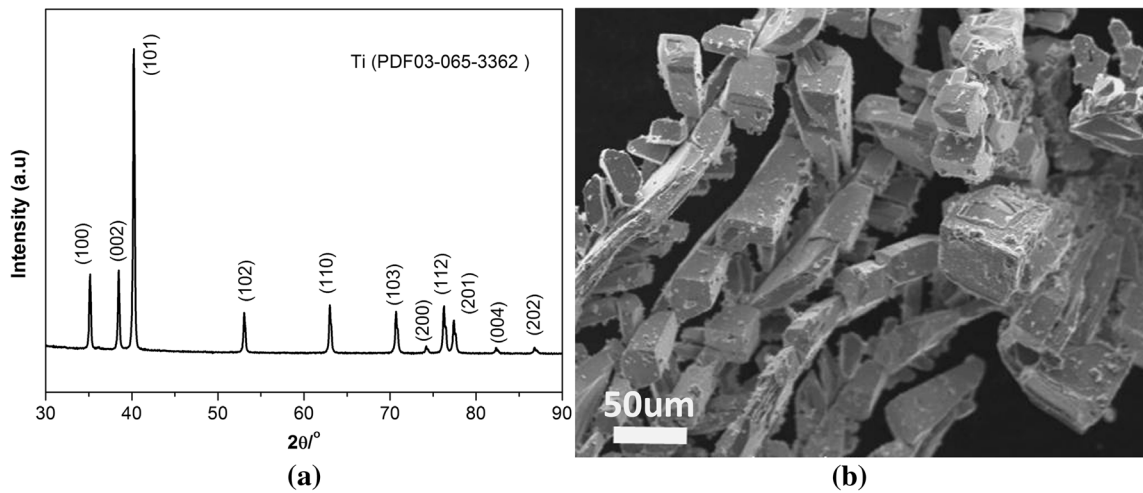


Fig. 4—(a) X-ray diffraction pattern and (b) SEM images of cathode deposit for investigation of its phase and surface morphology.

1073 K (800 °C). It can be observed that the current fluctuated around 0.15 A cm^{-2} for 1.5 h and then decreased to about 0.10 A cm^{-2} . The irregular surface of the sintered TiC anode can cause the current fluctuation. Meanwhile, the decrease in surface area of the TiC anode during the electrolysis process due to volume reduction arising from consumption of the soluble anode can also lead to the decrease of current. According to Faraday's law, the current efficiency of the electrolysis process is calculated and is 36.6 pct.

The deposit was then collected from the cathode substrate and cleaned ultrasonically in water and HCl (0.05 M) for further structural characterization. Its phase composition was analyzed with XRD. The corresponding pattern is shown in Figure 4(a). It can be observed that all diffraction peaks are indexed as standard diffraction peaks of metallic α -Ti (PDF 44-1294) with the space group of $P63/mmc$. No secondary phase is observed in the product. It has been reported that the phase transfer temperature between α -Ti to β -Ti occurs at around 1423 K (1150 °C).^[32] All experiments shown in the current work were performed at 1073 K (800 °C), and α -Ti was detected as the sole Ti phase. The sharp peaks at 40.23 and 38.48 deg, which are related to (101) and (002) planes in the hcp crystal structure of Ti, were used to calculate the grain size and the lattice parameter of the deposited α -Ti. According to Scherrer's equation, the grain size value of the produced titanium was measured to be 44 nm. The lattice parameters of α -Ti based on the strongest (101) peak were estimated to be $a = 0.2956 \text{ nm}$, $c = 0.4684 \text{ nm}$. These values are consistent with the previous report.^[33] The XRD results confirm the successful extraction of titanium with high crystallinity by molten salt electrolysis of the TiC anode in NaCl-KCl-1 mol pct TiCl_2 . In Figure 4(b), the surface morphology of deposited titanium is analyzed by SEM. It should be noted that dendritic titanium has formed, which may be attributed to the high current density in the electrolysis process. As reported by Bouchet,^[34] growth of dendritic metal is found in lithium ion batteries with a large concentration

gradient of ions in the electrolyte solution. Dendritic titanium was also produced in Takeuchi and Watanabe's work in case of large current density.^[21] In the current experiment, the relatively high current density of electrolysis likely leads to the high concentration gradient of Ti ions during electrolysis, which results in the inhomogeneous growth of titanium in different directions and thus formation of the dendritic crystal. However, the detailed formation mechanism of dendritic titanium is still unknown and requires further study.

To conclude, both the polarization curve and cyclic voltammograms show that titanium can be oxidized and dissociated from the TiC anode and dissolved into molten NaCl-KCl in the form of Ti^{2+} . The reduction/oxidation of Ti^{2+}/Ti in the molten salt is a one-step reaction. Titanium with high crystallinity was extracted successfully by molten salt electrolysis using the soluble TiC anode. Dendritic titanium with no impurities was obtained by potentiostatic electrolysis in molten NaCl-KCl-1 mol pct TiCl_2 . The current work advanced the understanding on the process of electrochemical oxidation and dissociation of titanium from the soluble TiC anode and reduction process of titanium ions in molten NaCl-KCl, and provided guidance for further investigation on titanium extraction by the molten salt electrolysis method.

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