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Formation of Ti or TiC nanopowder from TiO₂ and carbon powders by electrolysis in molten NaCl-KCl

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A new route to produce pure Ti powder or TiC nanopowder with diameters of ~50 nm by electrolysis in molten KCl–NaCl using TiO₂ and carbon powder was reported in this paper. This electrochemical experiment was carried out with an innovative equipment unitizing the chlorination and electrolyzation. A fine titanium powder was obtained after electrolysis at 4.0 V for 5 h at 850 °C. TiC nanopowder could be prepared in the anode chamber with the cell voltage up to 4.5 V. Furthermore, the product was analyzed using X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The results indicate that pure Ti or TiC nanopowder can be prepared after electrolysis. The TiC nanopowder exhibited a polymorphic structure, and it had good thermal stability and oxidation resistance below 345 °C in air investigated by TGA and DSC. Cyclic voltammograms were carried out and the electrode reaction mechanisms during the electrolysis process were discussed in the paper.

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1. Introduction

Titanium has attracted considerable attention as one of the most typical transition-metals.^{1,2} It has many excellent properties and the high strength, low density, and good corrosion resistance of titanium make it a desirable alternative to Al and steel for applications in aerospace and the marine vehicle industry.³⁻⁵ Titanium carbide as a transition-metal carbide is becoming a promising material due to its unique properties, such as high melting point, high hardness, high thermal and electrical conductivities, high mechanical stiffness, superior chemical and thermal stabilities, excellent wear resistance and catalytic activity.⁶⁻¹⁰ This advanced non-oxide ceramic material is widely used in industry, particularly as an abrasive material in the manufacture of sintered carbide plates for cutting tools, an enhancement agent for composite materials, and in the aerospace materials industry.^{7,11-13}

Due to the labor-intensive and cumbersome process of production of titanium by Kroll process (magnesium reduction), electrolysis in a molten salt system as a popular direction has been considered as more promising to replace Kroll process for producing titanium.^{14,15} Many novel methods based on electrolysis have been founded and developed, such as the electrolysis reduction of TiCl₄ (ref. 16 and 17) and the electro-deoxidation (FFC) process.^{15,18} However, the small solubility of TiCl₄ in molten chlorides and the low conductivity of TiO₂ cathode limit the developing of above two processes respectively. As a result, the calciothermic reduction (OS) process,^{19,20} and the composite anode electrolysis process (MER^{21,22} and USTB^{23,24}), *etc.*, have been

developed and make encouraging progress. But up until now, there are no commercial applications among those methods.

Recently, it has been reported that TiC powder could be synthesized by electrolysis in molten salt using TiO₂ and C.²⁵ Large and agglomerated TiC particles can be prepared by this method. However, the conventionally produced TiC is often contaminated with free carbon, particularly as nanopowder. TiC is easily oxidized, as a result, the residual carbons cannot be removed by oxidation and other methods.

Due to the Kroll process is composed of two step process, and the equipment is divided into independent reduction and electrolytic part, to simplify its process and equipment, a new route is developed to produce Ti or nanocrystalline TiC at a relatively low temperature with an innovative equipment unitizing the chlorination and electrolyzation in this study. Using TiO₂ and carbon powder as the raw materials, metallic Ti or polymorphic TiC powders can be prepared by electrolysis in NaCl-KCl melts at different cell voltage.

2. Experimental

The experimental apparatus for electrolysis is shown in Fig. 1. A corundum crucible (110 mm in diameter) with a hole (15 mm in diameter) in the bottom and placed on a molybdenum crucible (115 mm in diameter) was used as the cell. A cone-shaped molybdenum cathode was placed in the corundum crucible and connected to the molybdenum crucible. The molybdenum crucible was placed in a stainless steel crucible, which was located at the bottom of a stainless steel reactor. The hollow anode was made of graphite with a funnel-shape structure and many holes (3 mm in diameter) on its side face. The anode was

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Fig. 1 The schematic configuration of the equipment: (1) – electric furnace, (2) – reactor, (3) – stainless steel crucible, (4) – molybdenum cathode, (5) – corundum crucible, (6) – $TiO_2 + C$ pellets, (7) – molybdenum crucible, (8) – graphite anode chamber, (9) – aluminum silicate, (10) – insulating washer, (11) – stainless steel bar, (12) – DC power source, (13) – vacuum system.

connected to a stainless steel tube stretched out of the sealed stainless steel reactor.

Titanium dioxide (\geq 99.5%, Sinopharm Chemical Reagent Co. Ltd., China) and carbon powder (\geq 99%, Sinopharm Chemical Reagent Co. Ltd., China) were used in the present work to prepare the pellets placed in the graphite anode chamber. Titanium dioxide and carbon powders were weighed and mixed with a fixed molar ratio. The mixture was ball-milled for 8 h and made into pellets of 5–8 mm in diameter. Then, the pellets were dried at 120 °C for 48 h. After drying, the pellets were placed in the graphite anode chamber. NaCl (\geq 99.5%, Sinopharm Chemical Reagent Co. Ltd., China) and KCl (\geq 99.5%, Sinopharm Chemical Reagent Co. Ltd., China) were mixed in a composition of 75 mol% NaCl and 25 mol% KCl after vacuum drying completely. The mixture was packed in the corundum crucible and used as the electrolyte.

The stainless steel reactor was closed and sealed with insulating washer placed on the flange plane. Cooling water was poured into the jacket, after that, the apparatus was slowly heated to 350 °C under vacuum. Argon gas was flushed into the reactor until saturating it, and the reactor temperature was then ramped to 850 °C by 6 °C min⁻¹. Once the temperature was achieved and kept at 850 $^{\circ}$ C, the salt was melt for at least 20 min. Then, the graphite anode was lowered into the molten salt, and all the holes distributed on its side face were immersed under the level of electrolytes. An electric circuit was set up, and the electrolysis was conducted under a constant voltage of 3.5, 4.0 and 4.5 V, respectively. After electrolysis, the graphite anode was pulled out of the salt and cooled gradually to room temperature in the furnace. Finally, the graphite anode and the stainless steel crucible were removed from the reactor. The crude products were lifted from the molten salt and washed with distilled water to remove Na⁺, K⁺, and Cl⁻, and then the products were ultrasonically vibrated to remove the solidified salt. The samples were then dried in a vacuum oven at 50 °C for 24 h.

The phase compositions of the samples were identified using X-ray diffraction (XRD) measurements with a Cu-K α characteristic ray. The morphologies and structure of the samples were observed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The thermal oxidation behavior of the powders was investigated by simultaneous TGA/ DSC measurements in air atmosphere at a temperatureincrease rate of 5 °C min⁻¹.

3. Results and discussion

3.1 Stability investigation of TiO₂/C mixture

The effect of submerging the pellets in molten salt was investigated to confirm the starting material for electrolysis. Fig. 2 shows the XRD pattern of the pellet after immersion in NaCl-KCl molten salt at 850 $^{\circ}$ C for 4 h in argon atmosphere.



Fig. 2 XRD pattern of the pellet after immersion in NaCl–KCl molten salt.

Table 1 The thermodynamic data of the possible reactions involved the pellets and molten salts during the electrolysis process at 850 $^\circ\text{C}$

Number	Reaction	$\Delta G^{ heta}_{1123 m K}/$ kJ mol ⁻¹	$\Delta E^{ heta}_{1123~ m K}/$ V
(1)	$TiO_2 + 3C = TiC + 2CO$	149.443	
(2)	$TiO_2 + C = TiO + CO$	99.483	
(3)	$3\text{TiO}_2 + \text{C} = \text{Ti}_3\text{O}_5 + \text{CO}$	51.168	
(4)	$2\text{TiO}_2 + \text{C} = \text{Ti}_2\text{O}_3 + \text{CO}$	49.781	
(5)	$NaCl \rightarrow Na^{+} + Cl^{-}$		3.25
(6)	$KCl \rightarrow K^{+} + Cl^{-}$		3.38
(7)	$TiCl_4 \rightarrow Ti^{4+} + 4Cl^-$		1.63
(8)	$TiCl_3 \rightarrow Ti^{3+} + 3Cl^-$		1.65
(9)	$\text{TiCl}_2 \rightarrow \text{Ti}^{2+} + 2\text{Cl}^-$		1.84
(10)	$TiO_2 + 2C + 2Cl_2 = TiCl_4 + 2CO$	-281.93	
(11)	$2\text{TiO}_2 + 4\text{C} + 3\text{Cl}_2 = 2\text{TiCl}_3 + 4\text{CO}$	-277.105	
(12)	$TiO_2 + 2C + Cl_2 = TiCl_2 + 2CO$	37.918	
(13)	$TiO_2 + C + 2Cl_2 = TiCl_4 + CO_2$	-312.733	
(14)	$2\text{TiO}_2 + 2\text{C} + 3\text{Cl}_2 = 2\text{TiCl}_3 + 2\text{CO}_2$	-327.531	
(15)	$\mathrm{TiO}_2 + \mathrm{C} + \mathrm{Cl}_2 = \mathrm{TiCl}_2 + \mathrm{CO}_2$	7.125	

As evidenced in the Fig. 2, the phase composition of the sample pellets after the immersion experiment had no change except adherent NaCl and KCl salts. This result indicates that no reaction could occur only between TiO₂ and carbon during the process of electrolysis, which is consistent to the results of the positive $\Delta G_{1123 \text{ K}}^{\theta}$ value of reaction (1)–(4) shown in Table 1.

3.2 Influence of cell voltage

In order to determine the applied potential for the electrolysis, it is necessary to calculate the decomposition voltage. It can be seen from Table 1 that the decomposition voltages of NaCl and KCl are 3.25 and 3.38 V at 850 °C respectively, which are higher than the one of $TiCl_4$ (1.63 V), $TiCl_3$ (1.65 V) and $TiCl_2$ (1.84 V). It also can be concluded that the chloride of titanium can be reduced with decomposing NaCl and KCl. In order to determine the influence of the cell voltage on the electrolysis process, a constant voltage of 3.5, 4.0 and 4.5 V was applied respectively between the molybdenum cathode and the graphite anode full of the pellets with TiO_2/C molar ratio of 1 : 1 for 5 h at 850 °C. The vent gas was bubbled into water for 20 min since the beginning of the electrolysis. The pH of the water detected using PH indicator paper showed acidic. The solution was titrated with silver nitrate, as a result, white precipitate appeared. It shows that the vent gas contains Cl₂ certainly. The XRD patterns of the obtained sample on the cathode after washing are shown in Fig. 3.

From the XRD patterns as shown in Fig. 3, when the voltage of 3.5 V that was higher than the decomposition voltages of NaCl and KCl was applied, the Ti phase had been the main phase accompanied by $NaTi_2O_2$ in the product. The pattern of the sample after electrolysis at 4.0 V showed that the XRD peaks associated with the lower oxides, $NaTi_2O_2$ had completely disappeared, and only peaks associated with pure Ti were identified. With the voltage increasing to 4.5 V, the sample exhibited the diffraction peaks of the mixture of Ti and TiC. It was notable that there was anodic product appeared near the anode



Fig. 3 XRD patterns of the samples obtained on the cathode after washing in 850 $^{\circ}$ C NaCl-KCl melts after electrolysis at different cell voltage for 5 h.

chamber, and only peaks associated with pure TiC are observed in its XRD pattern as shown in Fig. 4.

Fig. 5 shows the SEM images and EDS spectra of the samples after electrolysis at different cell voltages. From the Fig. 5(a), combined with the result of the XRD data, the morphology of Ti and NaTi₂O₂ obtained at 3.5 V were of micron size. With the voltage increasing to 4.0 V, fine Ti powder was prepared. The spherical particles were dominant in the sample and the average grain size of Ti was about 2 μ m (Fig. 5(b)). As soon as the production of TiC started, spongy aggregate could be observed from Fig. 5(c). Fig. 5(d) shows the morphology of TiC obtained near the anode chamber after electrolysis at 4.5 V for 5 h in 850 °C NaCl–KCl melts. Interestingly, the rod-like and spongy aggregate morphology could be found in the figure. The EDS spectra (Fig. 5(e) and (f)) show that the product obtained at 4.0 V



Fig. 4 XRD pattern of the product prepared near the anode chamber with a TiO₂/C molar ratio of 1 : 1 after electrolysis at 4.5 V for 5 h in 850 $^{\circ}$ C NaCl–KCl melts.



Fig. 5 SEM images of the cathodic products in 850 °C NaCl-KCl melts after electrolysis at different cell voltages for 5 h ((a) 3.5 V, (b) 4.0 V, (c) 4.5 V) and the product prepared near the anode chamber at 4.5 V (d), EDS spectra (e) of the cathodic product obtained at 4.0 V (specture 1 in (b)) and EDS spectra (f) of the product prepared near the anode chamber at 4.5 V (specture 2 in (d)).

and 4.5 V was Ti and TiC respectively. The TEM images provide a direct view of the TiC sample as shown in Fig. 6.

Fig. 6(a) shows that the diameter of TiC particles is around 50 nm. Fig. 6(b) shows that the rod-like TiC has a spiral pattern, lattice fringes corresponding to the TiC (200) plane (d_{TiC} (200) = 0.20 nm) can be observed in the rod-like sample. Those results indicate that the TiC powders obtained after electrolysis at 4.5 V are the polymorphic mixture made up of nanoparticles and nanorods.

The stability of the TiC sample was evaluated by TGA–DSC analysis under air atmosphere, and the mass loss of the TiC sample *vs.* temperature during the heating is shown in Fig. 7.

The TiC powder shows an initial mass loss below 200 °C due to the loss of water. The weight loss remains almost constant between 200 °C and 345 °C, indicating that the TiC powder is stable in this temperature range. Then, a significant mass gain corresponding to a broad exothermic peak in the DSC curve occurred at 345 °C, which mainly originated from the oxidation of TiC at a low exothermic rate of reaction. When the temperature reached 550 °C, the slope of the TGA curve became smaller, probably because TiO₂ or TiN formed on the surface of TiC particles by the new phase prevented the diffusion of O₂ or N₂ into the interface of TiC and decreased the reaction rate. When the temperature exceeded 725 °C, the molecules moved rapidly, resulting in further oxidation or nitridation occurring at the



Fig. 6 Analytical TEM and HRTEM images of the TiC powders prepared at a TiO₂/C ratio of 1 : 1 after electrolysis at 4.5 V in 850 °C NaCl-KCl melts ((a) low-resolution TEM image, (b) high-resolution TEM image).



internal structure of the TiC particles. In this process, CO_2 was formed and adsorbed on the surface of the nanopowder. When the temperature exceeded 850 °C, those CO_2 was released, that resulted in weight loss. Finally, the sample was oxidized or nitrided completely at about 900 °C, and the weight gain remained almost constant in the TGA curve when the temperature was above 900 °C, indicating almost no weight change.

As described earlier, TiC is a potential candidate for hightemperature structural applications. However, in this study, the size of the TiC particles prepared by electrolysis is very small. Nanoparticles have large specific surface areas. Therefore, these TiC particles have a large surface energy, thus resulting in agglomeration with higher stability. In this study, the prepared sample was oxidized completely at around 900 °C. However, the sample has good thermal stability below 345 °C.

3.3 Discussing of the principle of the electrolysis process

The process using TiO_2 and carbon in NaCl-KCl melts to produce Ti can be divided into two main stages actually: electrolytic process and chlorination process. First, the electrolytic reaction of NaCl and KCl occur as reaction (5) and (6), and Cl₂ is prepared at the anode. Cl₂ can enter into the anode chamber through the graphite tube at the central position of the funnelshape anode. Then, the pellets made from TiO_2 and C can react with Cl_2 as reaction (10)–(15) in Table 1.

The results of thermodynamic calculation seen from Table 1 suggest that all the reactions might occur except reaction (12) and reaction (15) at 850 °C. The chlorination in Kroll process is according to reaction (12).¹⁴ However, in this paper, because of the chlorination taking place in molten KCl–NaCl, KCl or NaCl can form complex with TiCl₂ and TiCl₃ such as TiCl₃·KCl, TiCl₂·KCl, TiCl₃·NaCl and TiCl₂·NaCl.²⁶ As a result, the Gibbs free energies of eqn (14) and (15) are driving down. Furthermore, CO₂ is easier to be produced in molten chlorides.²⁷ Therefore, the chlorination reaction in the anode chamber can be described as following:

 $2\text{TiO}_2 + 2\text{C} + 3\text{Cl}_2 + 2\text{KCl} = 2\text{TiCl}_3 \cdot \text{KCl} + 2\text{CO}_2$ (16)

$$TiO_2 + C + Cl_2 + KCl = TiCl_2 \cdot KCl + CO_2$$
(17)

$$2\text{TiO}_2 + 2\text{C} + 3\text{Cl}_2 + 2\text{NaCl} = 2\text{TiCl}_3 \cdot \text{NaCl} + 2\text{CO}_2 \quad (18)$$

$$TiO_2 + C + Cl_2 + NaCl = TiCl_2 \cdot NaCl + CO_2$$
(19)

 $TiCl_3 \cdot KCl, TiCl_2 \cdot KCl, TiCl_3 \cdot NaCl and TiCl_2 \cdot NaCl also can be described as KTiCl_4, KTiCl_3, NaTiCl_4, NaTiCl_3, respectively. Consequently, those complex particles can be dissociated in melts:$

$$KTiCl_4 = K^+ + TiCl_4^-$$
(20)

$$KTiCl_3 = K^+ + TiCl_3^-$$
(21)

$$NaTiCl_4 = Na^+ + TiCl_4^-$$
(22)

$$NaTiCl_3 = Na^+ + TiCl_3^-$$
(23)

Then, titanium ions will enter into the melt and obtain electron at the cathode to produce metallic titanium.

To investigate the reaction mechanisms, cyclic voltammograns were carried out on a graphite working electrode with a groove full of the powders with TiO₂/C molar ratio of 1 : 1 in NaCl-KCl melts at 850 °C. The mass of the powders were 0.044 g. The cyclic voltammograms under different scanning rates of 25, 50, 75, 100 and 150 mV s⁻¹ are shown in Fig. 8(a). Three anodic waves A, B and C and three cathodic waves A', B' and C' are clearly visible in the curves. It can be confirmed that the cathodic wave A corresponds to chlorine evolution, while wave C corresponds to the deposition of sodium. Therefore, titanium deposition should be considered as occurs from 0.65 V to 0.30 V (wave B, vs. spectrum pure graphite). Small mass of the powders in working electrode leads to reduction wave B with low intensity. According to ref. 28 and 29, the number of exchanged electrons can be deduced from the cyclic voltammograms. For the titanium reduction peak, the plot of potential (V) vs. $\ln[I/(I_p$ (-I)] is linear and shown in Fig. 8(b). From the slope (RT/nF) of linear equation in Fig. 8(b), the exchanged electron number of titanium ions reduction is approximately equal to 3 ($n \approx 3$). So, it can be concluded that three electrons are exchanged in this



Fig. 8 Cyclic voltammograns in NaCl-KCl melts at 850 °C (a) and $\ln[I/(I_p - I)]$ as function of potential (b).

reduction. That is to say, the electrode reactions are according to the following equation,

Anodic reaction:
$$2Cl^{-} - 2e = Cl_2$$
 (24)

Cathodic reaction: $Ti^{3+} + 3e = Ti$ or $TiCl_4^- + 3e = Ti + 4Cl^-$ (25)

The theoretical charge (Q_0) is defined as the charge required in order to obtain 1 mol metallic Ti, and *F* is the Faraday's constant ($F = 96\ 485\ C\ mol^{-1}$).

As shown in eqn (25), Q_0 can be calculated as 3F. However, the cathodic reaction of the study of the electrolysis process using TiCl₄ to prepare Ti can be described as the following equation:

$$Ti^{4+} + 4e = Ti$$
 (26)

 Q_0 in this process is 4*F*, which is higher 1/4 than that in this paper. It indicates that the titanium production has significant improvement by the route in this paper compared to using TiCl₄ to prepare Ti. Furthermore, this new process can greatly reduce energy consumption when the electrolysis under the same conditions. The principle of the formation of metallic Ti from TiO₂ and carbon particles by electrolysis is shown in Fig. 9.

3.4 Formation of TiC

With the cell voltage up to 4.5 V, O^{2-} may be present in NaCl-KCl melts from the reduction of some TiO₂ placed in the anode chamber. Consequently, CO₂ is produced at the graphite anode combines with O^{2-} in the melt to form CO_3^{2-} , and then the CO_3^{2-} enters into the anode chamber and reacts with the pellets. As a result, TiC is prepared in the chamber as the following equation:

$$CO_2 + O^{2-} = CO_3^{2-}$$
(27)



Fig. 9 Principle of the formation of Ti from $TiO_2 + C$ pellet by electrolysis.

$$2\text{CO}_3^{2-} + 2\text{TiO}_2 + 5\text{C} - 4\text{e} = 2\text{TiC} + 5\text{CO}_2$$
 (28)

A part of TiC or carbon might drop to the cathode. Carbon powder also can react with the Ti prepared at the cathode as this:

$$Ti + C = TiC$$
(29)

Consequently, the powder obtained at cathode is the mixture of Ti and TiC at the cell voltage of 4.5 V.

4. Conclusions

In summary, metallic Ti or TiC nanopowder could be prepared by electrolysis in molten NaCl-KCl using TiO₂ and C powder with a new cell at different cell voltage. Fine Ti powder could be obtained at the cathode by electrolysis at 4.0 V in 850 °C NaCl-KCl melts for 5 h. Pure TiC nanopowder could be obtained at the anode chamber at 4.5 V. This improved design provides a new route to prepare Ti or TiC with good specific properties, and thus provides a new method to prepare other transitionmetal and its carbides.

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