Anodic Dissolution of Titanium Oxycarbide TiC$_{x}$O$_{1-x}$ with Different O/C Ratio

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The performance of TiC$_{x}$O$_{1-x}$ solid solutions with different O/C ratio serving as the anode in electrolysis cell was investigated in NaCl-KCl molten salt. It was found that the electrochemical dissolution occurs from the same potential for all the TiC$_{x}$O$_{1-x}$. The valance of the dissolved titanium ion depends on the potential applied. Both the dissolution ratio of titanium and the by-product of the anode reaction are dependent on the composition of the anode TiC$_{x}$O$_{1-x}$. For high carbon TiC$_{x}$O$_{1-x}$ ($x>0.5$), all the titanium in TiC$_{x}$O$_{1-x}$ dissolves as titanium ions with carbon monoxide (CO) and carbon (C) as the by-products. For low carbon TiC$_{x}$O$_{1-x}$ ($x<0.5$), carbon monoxide and carbon dioxide (CO$_2$) were detected in anodic gas, titanium partially dissolves as titanium ion and the remaining forms Ti$_2$O$_3$. The dissolution ratio of titanium decreases with the increase of oxygen in TiC$_{x}$O$_{1-x}$.

Titanium is considered to be an extremely valuable metal due to its excellent physical and chemical properties, such as high strength, toughness, durability, low density, corrosion-resistance and biological compatibility. Therefore, it has been widely used in medical treatments, aircraft and automotive production, chemical processing and others. However, the cost is extremely high due to the high cost of the current production method named Kroll process. The development of a titanium production process with low cost has attracted tremendous attentions from 1970s. Among the many alternative methods previously investigated, the electrolytic process is expected to be one of the most promising methods for titanium metallurgy, such as FFC-MER22 process. The USTB and MER processes are similar in the technical approach. Consumable anode is used in both processes. During the electrolysis, the titanium is dissolved as the titanium ion at the anode, and the titanium metal is deposited at the cathode from the molten salts bath. The difference between USTB and MER processes is in the anode material. In the MER process, the anode material is described as “composite”, the mixture of titanium sub-oxide and carbon (Ti$_{2}$O$_{3}$ + C), whereas in USTB process, compound of titanium oxycarbide, TiC$_{x}$O$_{1-x}$, is required for the consumable anode material. The titanium oxycarbide can be obtained from titanium dioxide by using carbotermal reduction route at temperatures higher than 1400°C. During the electrolysis process, the anodic reaction for TiC$_{0.5}$O$_{0.5}$ is

$$\text{TiC}_{0.5}\text{O}_{0.5} \rightarrow \text{Ti}^{4+} + 0.5 \text{CO} + n \text{e} \text{.}$$

The cathodic reaction is

$$\text{Ti}^{4+} + n\text{e} \rightarrow \text{Ti} \text{.}$$

The performance of TiC$_{0.5}$O$_{0.5}$ solid solutions with different O/C ratio serving as the anode in electrolysis cell was investigated in NaCl-KCl molten salt. It was found that the electrochemical dissolution occurs from the same potential for all the TiC$_{x}$O$_{1-x}$. The valance of the dissolved titanium ion depends on the potential applied. Both the dissolution ratio of titanium and the by-product of the anode reaction are dependent on the composition of the anode TiC$_{x}$O$_{1-x}$. For high carbon TiC$_{x}$O$_{1-x}$ ($x>0.5$), all the titanium in TiC$_{x}$O$_{1-x}$ dissolves as titanium ions with carbon monoxide (CO) and carbon (C) as the by-products. For low carbon TiC$_{x}$O$_{1-x}$ ($x<0.5$), carbon monoxide and carbon dioxide (CO$_2$) were detected in anodic gas, titanium partially dissolves as titanium ion and the remaining forms Ti$_2$O$_3$. The dissolution ratio of titanium decreases with the increase of oxygen in TiC$_{x}$O$_{1-x}$.

Experimental

TiC$_{x}$O$_{1-x}$ with different O/C ratio (TiC$_{0.7}$O$_{0.3}$, TiC$_{0.5}$O$_{0.5}$, TiC$_{0.45}$O$_{0.55}$, TiC$_{0.4}$O$_{0.6}$, TiC$_{0.33}$O$_{0.67}$ and TiC$_{0.2}$O$_{0.8}$) were synthesized from titanium monoxide (TiO, Beijing Mengtai Corp.) and titanium carbide(TiC, Beijing Mengtai Corp.) with different Ti:C:TiO ratio (7:3, 1:1, 9:11, 2:3, 1:2 and 1:4). Titanium monoxide and titanium carbide were homogenously mixed and pressed to form a pellet with 10 mm in diameter and 10 mm in height. The pellet was then sintered at 1600°C for 4 hrs under Ar atmosphere. The schematic diagram of the whole process is shown in Fig. S1.

The composition, crystal structure, and the morphology of the product before and after being sintered were analyzed by X-ray diffraction (XRD, JEOL JDX-3500, Cu Ka radiation) and scanning electron microscopy (SEM, JEOL JXA-8900M), respectively.

The electrochemical measurement was carried out in an equimolar NaCl-KCl solution (reagent grade, Beijing Chemical Industries). The salt was pre-dried in a graphite crucible under vacuum at the elevated temperature of 300°C for 4 hours to remove moisture. All electrochemical experiments were conducted in a sealed vessel under a dry helium atmosphere at 750°C.

The electrolysis and electrochemical experiments were performed using a potentiostat/galvanostat (EG&G PAR 263 A). A pellet of TiC$_{x}$O$_{1-x}$, with 3 mm in diameter is served as a working electrode, and a graphite (6 mm in diameter) rod is served as a counter electrode. The reference electrode was the Ag/AgCl electrode, which consisted of a silver wire (1 mm in diameter) in contact with the solution of AgCl (4 wt%) in a NaCl-KCl molten-salt mixture, contained in a Mullite tube. The reference electrode was calibrated against chloride evolution, and all the potentials were recorded with respect to the potential of Cl$_2$/Cl$^{-}$ electrode.

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During the potentiostatic electrolysis, the emitted gas from the anode was analyzed online using a mass spectrometer. Electrochemical experiments including linear polarization and square-wave voltammetry were performed under the same conditions as the electrolysis. For these measurements a tungsten disk electrode with 0.1 mm in diameter was used as a working electrode. The tungsten disk electrode was prepared by sealing a tungsten wire into a quartz tube, and polishing the bottom part as the electrode surface. A schematic diagram of the electrochemical cell and the tungsten disk electrode is shown in Fig. S2(a) and S2(b). The anodic gas generated during dissolution was monitored by mass spectrometer with a special instrument shown in Fig. S2(c) and (d). The TiC$_{x}$O$_{1-x}$ solid solution pellet was connected to a platinum wire as working electrode. A quartz sheath with 10mm in diameter and 50mm in height was used as a shell of the anode, and the anodic gas generated during the electrolysis was collected inside the shell. An alumina tube (3.2mm in diameter, 99.8%, McDanel Advanced Ceramic Technologies) with double bores (1mm in diameter) was used to hold the working electrode. One bore is used for the passing through of platinum wire as the current lead whereas the other one for the anodic gas to flow to the mass spectrometer. As shown in Fig. S2(c), some space between the quartz sheath and the alumina tube allows the helium gas to flow into the anode chamber. The anodic gas released during electrolysis was sampled through the alumina tube. The sampled anodic gas was analyzed for the concentration of CO, CO$_2$, and O$_2$ by online gas mass spectrum (MS, HPR20, Hiden Analytical).

**Results and Discussion**

XRD was used to provide composition and assignment of crystal structure information of TiC$_{x}$O$_{1-x}$. The XRD patterns of TiC$_{x}$O$_{1-x}$ with different O/C ratio are shown in Fig. 1a and Fig. S3. From Fig. 1a, it is clear that the peak positions of TiC, TiC$_{0.7}$O$_{0.3}$, TiC$_{0.5}$O$_{0.5}$, TiC$_{0.45}$O$_{0.55}$, TiC$_{0.4}$O$_{0.6}$, TiC$_{0.33}$O$_{0.67}$, and TiC$_{0.2}$O$_{0.8}$ shifted with the changing of O/C ratio in TiC$_{x}$O$_{1-x}$. With the increasing of O/C ratio in TiC$_{x}$O$_{1-x}$, the peaks shifted step by step from that of TiC to TiO. It indicates that all these TiC$_{x}$O$_{1-x}$ solid solution are formed after sintering, and they have the same structure as TiC and TiO. This is confirmed by the SEM analysis (Fig. 1, and Fig. S4).
It is evident that the average exchange electron number changes from higher than 0 V vs. Cl$_2$/Cl$^-$ on glassy carbon electrode gradually increases when the potential is polarization curves of Ti metal, TiC$_{0.7}$O$_{0.3}$, TiC$_{0.5}$O$_{0.5}$, TiC$_{0.45}$O$_{0.55}$, dissolution behavior as titanium metal. However, the slopes of anodic solutions under various potentials. The exchange electron number calculated according the square wave voltammograms is shown in Table 1.

It is evident that the average exchange electron number changes from 2.0 to 2.3 with the increase of electrolysis potential. This implies that TiC$_{0.1}$, has been dissolved into the melt during electrolysis mostly as Ti$^{2+}$ ions at −0.6 V, and partially as Ti$^{3+}$ when the electrode potential is raised. Clearly, the electrolysis potential demonstrated significant effect on the valence state of titanium ion, whereas the composition of TiC$_{0.1}$ (O/C ratio) does not provide any contribution to that of titanium ion. However, the O/C ratio might affect the anodic tail gas. According to our previous results, it was discovered that the anode reaction of TiC$_{0.5}$O$_{0.5}$ can be described as Eq. 1, during which Ti dissolves into chloride melt as TP$^+$ (n = 2–3), while C and O forms CO without any C or O left in anode. It would be ideal if during the anode reaction of TiC$_{0.1}$, with different composition (C/O ratio), all Ti dissolves as titanium ion, Ti$^{n+}$, while C and O leaves as C, CO, CO$_2$, and O$_2$ without any residual. Based on this ideal assumption, the anode reaction of TiC$_{0.1}$ could be described as follows, depending on the O/C ratio.

\[
\text{C}/\text{O} \leq 1, x \geq 0.5 \quad (\text{typically as TiC}_{0.05}\text{O}_{0.5} \text{and TiC}_{0.05}\text{O}_{0.5})
\]

TiC$_{0.1}$ $\rightarrow$ Ti$^{n+}$ + (1 - x)CO + (2x - 1)C + ne $\quad$ [3]

1 < O/C \leq 2, 0.33 \leq x < 0.5 \quad (\text{typically as TiC}_{0.05}\text{O}_{0.5}, \text{TiC}_{0.05}\text{O}_{0.6} \text{and TiC}_{0.33}\text{O}_{0.67})

TiC$_{0.1}$ $\rightarrow$ Ti$^{n+}$ + (3x - 1)CO + (1 - 2x)CO$_2$ + ne $\quad$ [4]

O/C > 2, x < 0.33 \quad (\text{typically as TiC}_{0.2}\text{O}_{0.8})

TiC$_{0.1}$ $\rightarrow$ Ti$^{n+}$ + xCO$_2$ + (1 - 3x)/2O$_2$ + ne $\quad$ [5]

To test the above assumption on the anodic dissolution mechanism, the anode gas during the electrolysis was analyzed by the mass

| Table 1. The valence of titanium ion after electrolysis of TiC$_{x}$O$_{1-x}$ at different potential. |
|-------------------------------------------------|------------------|------------------|------------------|
| Electrolysis Potential (V vs Cl$_2$/Cl$^-$)    | $-0.60$          | $-0.40$          | $-0.20$          |
| TiC$_{0.5}$O$_{0.5}$                            | 2.02             | 2.15             | 2.78             |
| TiC$_{0.4}$O$_{0.6}$                            | 2.08             | 2.21             | 2.83             |
Figure 4. The gas analysis result during electrolysis at −0.4 V vs Cl2/Cl−, (a) TiC0.7O0.3, (b) TiC0.5O0.5, (c) TiC0.45O0.55, (d) TiC0.4O0.6, (e) TiC0.33O0.67, (f) TiC0.2O0.8.

spectrometer online when the TiC0.1xO1−x was under electrolysis by applied a constant potential step. Figure 4 shows the monitored concentration of CO and CO2 in anode chamber before, during and after the electrolysis at the potential of −0.4 V vs Cl2/Cl−, for the TiC0.1xO1−x. In Fig. 5, the average concentration of CO and CO2 during the electrolysis is plotted against the applied potential. CO was the only anode gas during dissolution for TiC0.7O0.3 and TiC0.5O0.5. With the change of O/C ratio in TiC0.1xO1−x, both of CO and CO2 were detected for TiC0.45O0.55, TiC0.4O0.6, TiC0.33O0.67 and TiC0.2O0.8. During the electrolysis of all TiC0.1xO1−x solid solution, no O2 was found in the anodic gas. It is important to note that both CO and CO2 were found simultaneously even at very low potential. The concentrations of both CO and CO2 in the anode increase with the increase of the applied potential. This corresponds well with the current rise in the polarization curve in Fig. 2. As we only see the gas generation of CO in TiC0.7O0.3 and TiC0.5O0.5, the anodic reaction of high carbon content TiC0.1xO1−x (O/C ≤ 1, x ≥ 0.5) most likely follow the Eq. 3. However, for the high oxygen content TiC0.1xO1−x (O/C > 2, x < 0.33), the anode reaction obviously does not follow the Eq. 5 since we have never seen O2 generation. In the middle range of carbon content, 1 < O/C ≤ 2, 0.33 ≤ x < 0.5, both CO and CO2 were detected, corresponding with Eq. 4. However, the concentration of CO2 in the anode gas was far lower than that of CO. CO was always the major component in the anodic gas in the entail range of oxygen content in TiC0.1xO1−x, even for...
Figure 5. The potential dependence of the anode gas concentration during the electrolysis of TiC\(_{x}\)O\(_{1-x}\): (a) TiC\(_{0.7}\)O\(_{0.3}\), (b) TiC\(_{0.5}\)O\(_{0.5}\), (c) TiC\(_{0.45}\)O\(_{0.55}\), (d) TiC\(_{0.4}\)O\(_{0.6}\), (e) TiC\(_{0.33}\)O\(_{0.67}\), (f) TiC\(_{0.2}\)O\(_{0.8}\).

TiC\(_{0.33}\)O\(_{0.67}\) and TiC\(_{0.2}\)O\(_{0.8}\). Obviously, for the high oxygen content TiC\(_{x}\)O\(_{1-x}\) (O/C > 1, x < 0.5) part of oxygen content does not leave as the gas product.

In Fig. 6a the concentration ratio of CO\(_2\) to CO in anodic gas is shown as the function of the applied potential during the electrolysis. It is interesting that the CO\(_2\)/CO ratio is always kept around the same value for a certain carbon (oxygen) content TiC\(_{x}\)O\(_{1-x}\), regardless of the applied potential. However, the O/C ratio in TiC\(_{x}\)O\(_{1-x}\) played a significant role on the CO\(_2\)/CO ratio in the anodic gas. CO\(_2\)/CO ratio increases with the increase of O/C ratio in TiC\(_{x}\)O\(_{1-x}\) anode material itself. In Fig. 6b, O/C ratio in anodic gas (CO, CO\(_2\)) is plotted as the function of the O/C ratio in TiC\(_{x}\)O\(_{1-x}\) anode material. In this figure, the blue dot line shows the theoretical value if the anode reaction follows the Eqs. 3–5. Other than the point of O/C = 1:1, the O/C ratio in anodic gas is always smaller than that in TiC\(_{x}\)O\(_{1-x}\) anode material, and such deviation becomes even larger as the ratio increases further. This implies that O in TiC\(_{x}\)O\(_{1-x}\) is consumed incompletely in the range of O/C ratio higher than 1:1. In order to analyze the by-product other than the gas species during the anode reaction, a four-hour electrolysis was carried out on TiC\(_{0.7}\)O\(_{0.3}\), TiC\(_{0.5}\)O\(_{0.5}\), TiC\(_{0.4}\)O\(_{0.6}\), and TiC\(_{0.2}\)O\(_{0.8}\).
The O/C ratio in anodic gas for different TiC compositions. On the other hand, the anode material composition, and O/C ratio in TiC shows the significant effect on the anode gas composition. As seen in Fig. 6a, the concentration ratio of CO to CO is not potential dependent, but is a function of composition of the anode TiC. Figure 8a shows CO2/CO ratio as the function of O (TiO) concentration in TiC. The CO2/CO ratio increases almost linearly with O concentration in the anode material. The dissolution ratio, z, can be calculated from the CO2/CO ratio, and is shown in Fig. 8b. The dissolution ratio decreases linearly with the increase of the oxygen content.

Conclusions

TiC solid solutions with different O/C ratio demonstrated the similar dissolution behavior under electrolysis in NaCl-KCl. During the electrolysis, Ti was dissolved into molten salt as titanium ion, Ti, and the valence of the dissolved titanium ion, n, is dependent on the applied potential. Carbon and oxygen were released as carbon, carbon monoxide and carbon dioxide depending on the O/C ratio in TiC. For high carbon content TiC (x≥0.5, O/C≤1), all titanium dissolved as the titanium ion, whereas carbon and carbon monoxide CO were the by-products of the anode reaction. For low
carbon content TiC\textsubscript{x}O\textsubscript{1-x} (x<0.5, O/C>1), the anode gas contained CO and CO\textsubscript{2}, most of the titanium dissolved as titanium ion, whereas part of titanium formed as Ti\textsubscript{2}O\textsubscript{3} without dissolution. For the same content, TiC\textsubscript{x}O\textsubscript{1-x}, the concentration ratio of carbon dioxide to carbon monoxide, CO\textsubscript{2}/CO, stayed constant regardless of the applied potential. With the increase of O in TiC\textsubscript{x}O\textsubscript{1-x}, the CO\textsubscript{2}/CO ratio increases and the dissolution ratio of titanium as titanium ion, z, decreases linearly.

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Figure 8. (a) The ratio of CO\textsubscript{2} to CO in anode gas, (b) The dissolution ratio of TiC\textsubscript{x}O\textsubscript{1-x}, as the function of the oxygen content in TiC\textsubscript{x}O\textsubscript{1-x} solid solution.