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Electrolysis of Ti₂CO solid solution prepared by TiC and TiO₂

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Abstract

TiO₂ can be reduced by TiC at temperatures in excess of 1000 °C, under vacuum conditions. The resulting product was found to show the structures of a Ti_2CO solid solution, which has excellent conductivity like a metal. A series of experiments have been performed on the possibility of titanium electrolysis, using a Ti_2CO solid solution as an anode, in a NaCl–KCl melt. Carbon monoxide (CO) was monitored at the anode during electrolysis when the potential was kept constant. The product on the cathode was analyzed using scanning electron microscopy (SEM) and X-ray diffraction (XRD). The results show that titanium powders can be prepared through electrolysis of a Ti_2CO solid solution. The oxygen content of the titanium powders was measured and the result shows that it is lower than 300 ppm. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

Titanium and titanium alloys have attracted much attention because of their many applications, including in corrosion protection, electrode for metal production and for producing shape memory alloy, etc. The primary titanium metal, spongy titanium, is currently produced industrially by a process invented by Kroll [1]. The Kroll process is a batch method including two steps, involving the conversion of titanium oxide to titanium tetrachloride and titanium tetrachloride reduction by pure magnesium metal. The specific cost of titanium metal produced by the Kroll process is maintained high due to the expensive steps required to obtain the metal.

Since the early 1970s, the research focus of the titanium industry has been directed towards developing a continuous process to produce high purity titanium, with a low production cost [2–8]. Many kinds of alternative methods have been investigated. Electrolysis, the extraction and preparation of pure metal from ores using an electrolytic process, is considered as a promising method for titanium metallurgy [4–8]. Recently, several electrolysis and relative methods such as the FFC Cambridge process [9–13] and calciothermic reduction [14–17] have been investi-

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gated due to their potential for decreasing the cost of titanium production.

It is well known that both titanium carbide (TiC) and titanium monoxide (TiO) have the same cubic structure and space grouping, and a similar lattice size, so they are capable of forming a continuous series of solid solutions. Wainer et al. obtained the mutual solid solution of titanium carbide and titanium monoxide through dissolving titanium carbide and titanium monoxide using an arc temperature in excess of 2000 °C [18,19]. The solid solution can be extracted to form the titanium ion in the molten salt, using the electrolysis conditions. The carbon and oxygen component in the solid solution will liberate to form the CO gas.

This work presents a continuous electrolysis process for producing pure titanium. A Ti₂CO solid solution prepared by TiO₂ and TiC at a temperature in excess of 1000 °C, and this was used as an anode in NaCl–KCl melt. Carbon monoxide was monitored on the electrode during the electrolysis when the potential was kept constant. Furthermore, pure titanium metal was obtained on the cathode.

2. Experimental details

TiO₂ and TiC powders of reagent grade were mixed with the mole ratio of 1:2 and pressed at 300–1000 kg cm⁻² into a bar. The bar was sintered at various temperature from 600 °C to 1200 °C, under vacuum (<100 Pa) for 4 hours. The chloride salt mixture NaCl–KCl was melted in an alumina crucible placed within a hermetic alumina tube inside a furnace controlled by a CHINO DZ3000

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programmable device. The molten salt mixture was dehydrated under flowing argon at 300 °C and then fused under an argon atmosphere at 800 °C. The melt temperature was measured using a thermocouple protected by an alumina tube.

Electrochemical experiments were performed with a potentiostat/galvanostat (EG&G Princeton Applied Research, Model 263A). The reference electrode was a Ag/AgCl electrode. This consists of a silver wire with a 1 mm diameter immersed in a NaCl–CsCl molten mixture containing 4 wt.% silver chloride, contained in a mulite tube. The potential of the reference electrode was calibrated against Cl_2/Cl^- electrode generated by currentstatic electrolysis on a graphite bar. A potential range of -1.0 V to -0.2 V versus Cl_2/Cl^- reference was used to perform potentiostatic electrolysis. A gas chromatograp (Hewlett packard 5880 A series) was applied to monitor the anode gas. The structure and morphology of the cathode product was analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

3. Results and discussion

TiO₂ and TiC powders were mixed homogenously and pressed to form pellets with diameter of 20 mm and height of 10 mm. The pellet herein before was sintered at various temperatures. XRD analysis was used to study the structure of the sintered pellets, and the corresponding result is shown in Fig. 1. In the pellets sintered at 600 °C, there still remains strong peaks of raw materials (TiO₂ and TiC), while in the pellets sintered at 1000 °C, peaks for TiO₂ almost disappear. Those results indicate that the reduction reaction of TiO₂ by TiC happens at temperatures higher than 1000 °C. The reduction reaction of TiO₂ to TiO by TiC could be described as,

$$2\text{TiO}_2 + \text{TiC} \rightarrow 3\text{TiO} + \text{CO}(g)$$
 (1)

The reaction equilibrium constant of the reaction, $K_1 = Pco$, could be calculated from the standard free energy of the compounds involved, and the results of K_1 , at 600, 1000 and 1200 °C, are 1.4×10^{-11} , 2.9×10^{-5} and 2.7×10^{-3} , respectively. Obviously, it should be impossible to reduce TiO₂ by TiC to pure TiO through equation (1), at 1000 °C and even at 1200 °C, under the vacuum level of this research (10^{-3} atm.). However, our experimental results clearly demonstrated the progress of the reduction at the temperatures higher than 1000 °C. This phenomenon may



Fig. 1. XRD traces of the prepared products at various temperatures using TiC and TiO₂ as reactants.



Fig. 2. A typical current to time profile performed using an electrolytic potentiostatic value of -0.45 V vs. Cl₂/Cl⁻.

Table 1	
The anode gas concentration at different potential conditions	

Potential (V) (vs. Cl ₂ /Cl ⁻)	Anode gas component (ppm)		
	СО	CO ₂	
-1.0 (rest)	0	0	
-0.65	600	0	
-0.45	4300	0	
-0.25	7600	0	

result from the formation of compound or solid solution structure of TiO with TiC (TiC·TiO), which reduces the activity of TiO sharply and promotes the reaction. Therefore, the product of the reduction is not pure TiO but the solid solution. In fact when we start from the mole ratio of 1:2 for TiO₂ and TiC, the product formation is Ti₂CO. To further present this variation, the conductivity of the sintered pellets sharply increase (>10,000 times), which might be because of the changing crystal structure from titanium dioxide to a Ti₂CO solid solution.

The pellets of the Ti_2CO solid solutions were used as the anode, carbon steel as the cathode and a Ag/AgCl electrode as the



Fig. 3. Typical square wave voltammograms for background (solid line) and titanium ion dissolved from the Ti_2CO solid solution (dot and solid line) in NaCl–KCl melt.

reference electrode. Potentiostatic electrolysis was performed in NaCl–KCl molten salt at 800 °C. Gas-spectra apparatus was used to measure the off-gas. The relationship between time and current is presented in Fig. 2.

Table 1 shows the concentrations of the anode gas at the same sampling time when various electrolysing potentials were applied. It was found that CO gas was produced during electrolysis, and the concentration of it increased with increasing potential until chlorine gas evolution started. The phenomenon may result from the electrochemical extraction of carbon and oxygen at the anode potentials.

Titanium carbide has been used as a consumable anode to obtain highly pure titanium. However, carbon residue from the TiC anode disturbed the continuous electrolysis. In contrast, in the case of the solid solution anode, the carbon component of the solid solution anode can be extracted as carbon monoxide gas with the oxygen component. The titanium component of the anode was thought to dissolve into the molten salt as a titanium ion. In order to confirm this expectation, the experiment was carried out by using a used melt. A tungsten microdisk electrode with a diameter 0.1 mm was used as working electrode, a graphite bar with a diameter of 6 mm as the counter electrode and the same Ag/AgCl reference electrode as detailed above.





Fig. 4. The SEM image (a) and XRD trace (b) of electrodeposited product at the cathode.

Fig. 3 shows the result obtained by a negative potential sweep through square wave voltemmetry. One wave appears at a potential of -1.6 V versus Cl⁻/Cl₂. This wave is responsible for the reduction of the titanium ion dissolved into the melt during potentiostat electrolysis. A well Gaussian shape will be beneficial to calculate the exchanging electron number of the electrochemical reduction from the width of the wave, according to the theory of Osteryoung et al [20]. The wave width was obtained by curve fitting with Guanssian peak, and resulting the electron number of 2.07. That means that the titanium ion dissolved by the anode electrolysis is Ti²⁺.During the electrolysis, titanium deposit happens on the cathode. The pure titanium was obtained on the cathode by constant current electrolysis on a steel bar with a diameter of 6 mm for several hours. Fig. 4a shows the morphology of the titanium powder. A grain size of more than 40 µm was found. Fig. 4b presents the XRD trace of powder electrodeposited on the cathode, and it can be seen that the powder shows the crystal structure of pure titanium. Oxygen content of the cathode product was measured and the result showed that it was lower than 300 ppm.

4. Conclusion

Ti₂CO solid solution was prepared through the reaction of TiO₂ and TiC at temperatures in excess of 1000 °C, under vacuum conditions. The solid solution obtained shows excellent conductivity. A series of experiments have been conducted on the possibility of titanium electrolysis using a Ti₂CO solid solution as an anode. Carbon monoxide CO evolved at the anode was monitored during the electrolysis when the potential was kept constant. The product on the cathode was investigated by scanning electrode microscopy with EDS, and X-ray diffraction. The results show that titanium powders can be prepared through electrolysis of a Ti₂CO solid solution. Oxygen content of the titanium powders was measured and it was lower than 300 ppm.

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