

Electrolytic Reduction of Titania Slag in Molten Calcium Chloride Bath

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Ferro-titanium is prepared by direct electrolytic reduction of titania-rich slag obtained from plasma smelting of ilmenite in molten CaCl_2 . The product after electro-reduction is characterized by x-ray diffraction, scanning electron microscopy, and electron probe microanalysis. The electrolysis is carried out at a cell voltage of 3.0 V, taking graphite as the electrolysis cell as well as the anode, and a titania-rich slag piece wrapped by a nichrome wire is used as the cathode.

INTRODUCTION

Titanium and its alloys have unique properties, such as low-density, high-specific strength, high-temperature strength, and exceptional resistance to corrosion. Because of these properties, titanium and its alloys find a wide variety of industrial applications of which the important ones are in the aerospace, automobile, and chemical industries.¹ Among all the alloys of titanium, ferrotitanium, an alloy of iron and titanium, is basically used in steel making as a cleaning agent for iron and steel. It is known that titanium is highly reactive toward sulfur, carbon, oxygen, and nitrogen. Hence, it is used in steel making to remove the above-mentioned impurities.² Apart from this, the most important use of this alloy is as a hydrogen storage material. Hydrogen has recently been found to be the most challenging alternative to fossil fuels. However, a hydrogen economy requires an infrastructure to deliver hydrogen from where it is produced to the point of end use (i.e., a suitable storage material).³

The starting materials for the production of ferrotitanium are ilmenite, leucoxene, perovskite, and slag concentrates produced from ilmenite. Different methods have been adopted to produce ferrotitanium such as carbon reduction and metallothermic reduction.³ The carbothermic reduction of ferrotitanium results in a high carbon content in the material. However, as the use of ferrotitanium is to combine with the carbon in steel, the presence of carbon in the ferrotitanium is undesirable. Therefore, this production method is not commonly used. In the aluminothermic production of ferrotitanium,

there is a high consumption of aluminum, as it reacts both with the iron oxide in the ilmenite and with the oxygen-producing substances added to increase the exothermicity.⁴

Looking on to these aspects, the direct electrolytic reduction of titania-rich slag provides a simpler method for production of ferrotitanium alloy.⁵⁻⁷ Actually, plenty of crude titania slag is produced industrially by the carbothermic reduction of hemo-ilmenite or ilmenite ore concentrate. Also, titania slag exhibits a semiconductive behavior.⁸ Its good electronic conductivity of 10 S/m is a result of the sub-stoichiometric titanium oxide it contains. These oxides exhibit the typical Andersson-magnelli crystal structure having the chemical formula $\text{Ti}_n\text{O}_{2n-1}$, with n an integer at least equal to 4 (e.g., Ti_4O_7 , Ti_5O_9 , and Ti_6O_{11}).

The article reports on the studies related to the production of titanium metal and alloy by direct reduction of titania-rich slag in molten calcium chloride.

EXPERIMENTAL

Titania-rich slag was prepared by plasma smelting of ilmenite. The slag piece was wrapped with a nichrome wire to be used as cathode during electrolysis. Anhydrous CaCl_2 (AR grade) was used as electrolyte.

The electrochemical experiments comprised the pretreatment of the calcium chloride as well as the actual deoxidation of titania-rich slag. The pretreatment consisted of heating of the calcium chloride at 200°C for 12 h and pre-electrolysis of the molten calcium chloride, to eliminate redox-active species

and moisture. A suitable quantity of anhydrous calcium chloride (Qualigens, India), usually between 700 g and 800 g, was placed in a graphite crucible that also served as the anode. The calcium chloride salt was dried by properly heating at 200°C for 12 h. Then the temperature was raised to 950°C. The slag sample wrapped with nichrome wire was inserted into the CaCl_2 mass so that the slag piece remained totally immersed in it. A stainless steel rod was also inserted into the CaCl_2 for pre-electrolysis purpose.

Pre-electrolysis

Pre-electrolysis was carried out by applying a direct voltage of 2 V between the graphite crucible (anode) and a stainless steel rod (cathode) until a small and time-independent current was established.

Electrolysis

The electrolysis was done at a voltage of 3 V. The duration of electrolysis is 18–24 h. After electrolysis, the reaction chamber was allowed to cool. The graphite crucible was taken out of the inconel pot, and the solidified salt was dissolved in water. The reduced sample along with the nichrome wire was taken out of the crucible. The reduced product was detached from the wire and kept under cold water for 3–5 h; then it was washed with acetone, air-dried, and gently rubbed with emery paper to remove impurities from its surface. The morphology, structure, and composition of the electrolytic product was analyzed by scanning electron microscopy (SEM), energy-dispersive x-ray (EDX) (JEOL model), and x-ray diffraction (XRD; Philips PW3020 Xpert model). The electron probe microanalysis studies of the samples at different points using the super probe JXA 800 electron probe microanalyzer (EPMA; JEOL) were also carried out.

RESULTS AND DISCUSSION

The slag appeared irregular with numerous small cracks. It was highly porous. The x-ray fluorescence (XRF) analysis of the sample showed 77% TiO_2 and 17.5% Fe. Apart from these, Al, Mg, Si, and so on are found in small quantities.

After electroreduction and washing, the sample retained its shape and it was black in color. Also, slight shrinkage in the electrolyzed slag piece was observed. After rubbing with the emery paper, it showed a grayish metallic luster. A typical current–time plot for 24 h electrolysis of the slag sample is shown in Fig. 1, which shows a high initial reduction current attributed to oxygen removal from the slag. In comparison with the current–time plot for TiO_2 reduction (Fig. 2), a higher initial reduction current is observed in the present case. This may be from the higher electronic conductivity of the slag sample as a result of the presence of different conducting magnell phases. The XRD pattern of the reduced sample is shown in Fig. 3, which shows

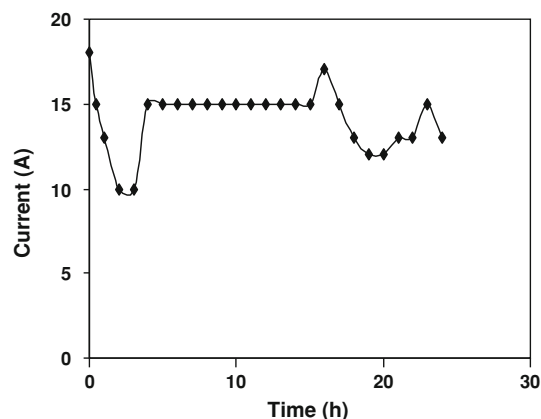


Fig. 1. Current-time plot for titania-rich slag electrolysis.

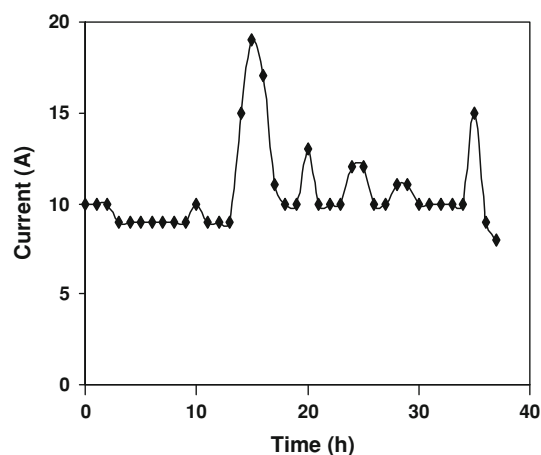


Fig. 2. Current-time plot for TiO_2 pellet electrolysis.

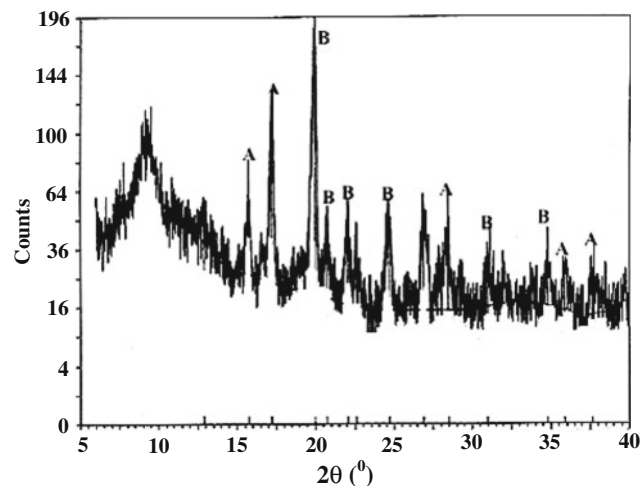


Fig. 3. XRD pattern of the slag sample after 24 h of electrolysis in molten CaCl_2 at 950°C.

major peaks of ferrotitanium (FeTi) in addition to Ti. The microscopic studies (Fig. 4) show the morphology of the product revealing a fiber-like

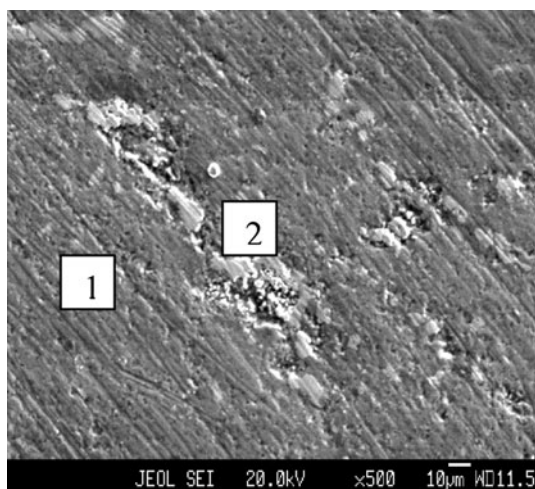


Fig. 4. SEM micrograph of electrolysed titania-rich slag.

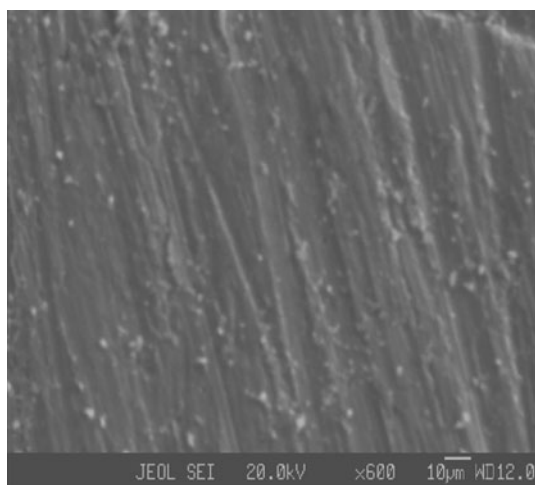


Fig. 5. SEM micrograph of pure Ti metal.

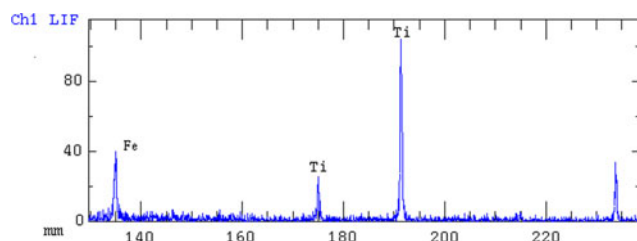


Fig. 6. WDS graph corresponding to point 1 of Fig. 4.

structure that is quite similar to that of the pure titanium metal shown in Fig. 5. However, the fibrous structure is not uniform. The WDS graph (Fig. 6) corresponding to point 1 in Fig. 4 shows Ti as the major metallic component in addition to Fe. Point 2 in the same sample (Fig. 7) shows Fe as the major metallic component followed by Ti. EPMA analysis of the sample in Fig. 4 shows the presence of minute quantities of other metallic elements such as Si and Al in addition to Ti and Fe. However,

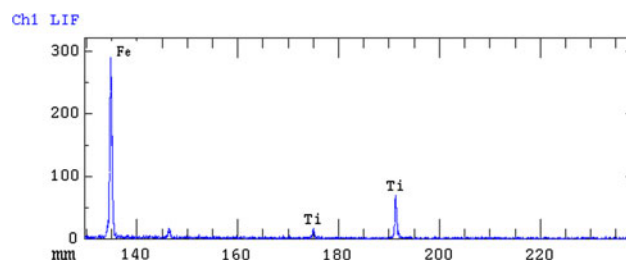


Fig. 7. WDS graph corresponding to point 2 of Fig. 4.

impurities in the slag sample such as Ca and Mg are not found in the electrolysed product. The retention of Si and Al may be a result of the electrochemical reduction of silicates and alumina to Si and Al, respectively.^{9,10}

CONCLUSION

This method provides a very simple method for preparation of ferrotitanium directly from titania-rich slag. Also, the good electronic conductivity of the titania-rich slag facilitates the electrolysis process. In the reduction process, there is no need to prepare a compact electrode as in TiO_2 electrolysis because the slag piece can be directly used as an electrode. Also, the electrolysis helps in removal of impurities such as Ca and Mg.

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