



Production of Fe–Ti alloy from mixed ilmenite and titanium dioxide by direct electrochemical reduction in molten calcium chloride

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ABSTRACT

It is important to develop technologies for the production of high-purity metals and alloys for industrial applications. With the aim of addressing the urgent problem of depletion of resources and the commercial challenges associated with the development of new technologies, detailed research on the electrolysis of mixed FeTiO₃/TiO₂ in a molten CaCl₂ electrolyte was conducted to prepare a high-purity, and high-opacity ferrotitanium (Fe–Ti) intermetallic alloy. Mixed solid oxides of FeTiO₃ and TiO₂ with FeTiO₃:TiO₂ molar ratios of 2.78:1.00 and 0.58:1.00 were used for the preparation of Fe–Ti intermetallic alloys (required molar ratios: Ti:Fe = 1.36:1.00 and 2.72:1.00). A mixed solid oxide of FeTiO₃ and TiO₂ was reduced electrochemically in a molten CaCl₂ electrolyte at 950 °C and a constant voltage of 3.0 V. The metallic samples formed by the electrochemical reduction were analyzed using X-ray diffraction, scanning electron microscopy/energy-dispersive X-ray spectroscopy, electron-probe microanalysis, inductively coupled plasma atomic-emission spectroscopy, ion chromatography, and oxygen and carbon analyzers. The mixed oxide pellets were strongly and successfully reduced to a high-purity Fe–Ti intermetallic alloy of β-Ti (FeTi₄) and FeTi phases of high-opacity and with small amounts of detected impurities.

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1. Introduction

Ferroalloys are master alloys containing other elements; they have limited solubilities in molten iron and improve the properties of iron and steel. These alloys usually contain significant amounts of iron. Ferroalloys have been used for the last 100 years, principally in the production of cast-iron and steel. Ferrotitanium (Fe–Ti) is a master alloy containing at least 28% titanium, and it is obtained by reduction of the corresponding raw materials or their concentrates. Compared with pure titanium, Fe–Ti has the advantages of better solubility and a lower price [1,2].

The starting materials for the production of Fe–Ti are ilmenite, leucoxene, perovskite, and slag concentrates produced from ilmenite. Because of the increasing availability of titanium scrap, this is also used to an increasing extent for the production of Fe–Ti.

Ilmenite (FeTiO₃) is a naturally occurring, abundant, and economically important mineral. Since its discovery, FeTiO₃ has grown greatly in importance. It is the most important titanium ore. Titanium was at one time a metal with few uses and, basically, no one knew how to make use of it. Until it was finally shown that the

metal could be produced commercially, it was considered to be a laboratory curiosity. Since then, titanium has been shown to be a strong metal, like aluminum (Al), light-weight, non-corrosive, and with very good strength.

Most FeTiO₃ is mined for TiO₂ production. Finely ground TiO₂ is a bright white powder widely used as a base pigment in paints, papers, and plastics. As sources of high-grade titanium minerals decrease worldwide, processes involving low-grade minerals such as FeTiO₃ are attracting much more attention. However, because of the high content of impurities, especially iron oxides, refining is necessary to obtain titanium-rich material or to make Fe–Ti alloys. The extraction of titanium from FeTiO₃ is highly energy intensive and tedious, and this accounts for its high market price and restricts its uses. An obvious solution is to make Fe–Ti alloys instead of titanium.

A Fe–Ti alloy containing 70% titanium and 30% iron falls at the eutectic point of the system, with a melting point of 1085 °C, and is therefore known as eutectic Fe–Ti. This temperature is well below steel-making temperatures, and metallic titanium can enter the steel far more quickly from Fe–Ti alloy melts than it can by dissolution. Eutectic Fe–Ti is therefore the preferred candidate for use in steel-making [2].

Generally, ferroalloys are prepared by reduction of oxide ores or concentrates with carbon (carbothermic), silicon (silicothermic), or aluminum (aluminothermic). The production and use of titanium as a large-volume construction material yields enough scrap for

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Fe–Ti containing 70% titanium to be made by melting iron and titanium scraps together. Fe–Ti production can be carried out using carbothermic or aluminothermic processes [2–4].

Carbothermic production in an electric arc furnace leads to high carbon contents in the Fe–Ti. However, as the main use of Fe–Ti is to combine with the carbon in steel, the presence of carbon in the Fe–Ti is undesirable. This production method is therefore now rarely used. Carbothermic processes for the production of Fe–Ti have been largely replaced by metallothermic processes, mainly aluminothermic.

As the availability of titanium scrap is increasing with the growth in titanium consumption, scrap is being increasingly used for the production of Fe–Ti. Because of its low melting point (1085 °C), the alloy containing 70% titanium melts comparatively readily when alloyed with iron in an induction furnace, in an arc furnace with consumable electrodes under vacuum or argon, or in an electro-slag-melting furnace.

The recent demonstration of direct electrochemical reduction of solid metal oxides in molten salts promises a novel generic technology, not only for the extraction of reactive metals such as titanium, but also for the synthesis of many functional alloys, intermetallics, and inorganic materials. As an attractive functional material, Fe–Ti alloy has been gaining increasing attention since it was first developed. It has excellent hydrogen-storage abilities and a low expansion rate. It therefore has potential for use as a solid hydrogen-storage material. Hydrogen is an ideal energy carrier, and is considered to be suitable for future transport applications, such as automotive applications. Hydrogen storage is one of the key challenges in developing a hydrogen economy. Hydrogen can be stored as (i) a pressurized gas, (ii) a cryogenic liquid, or (iii) a solid fuel, in chemical or physical combinations with materials, such as in metal hydrides or complex hydrides [5].

In this context, the preparation of Fe–Ti alloys has become a more important research topic. It is also important to produce Fe–Ti alloys using more economical processes than the traditional carbothermic or aluminothermic reduction process. We therefore tried to prepare Fe–Ti alloys using electrochemical reduction processes, as these require fewer processing steps, have low labor requirements, can reduce combinations of different metal oxides to form alloys, and are environmentally friendly.

Since the novel molten salt electrolysis process known as the Fray, Farthing, and Chen (FFC) process was first reported, it has been used to prepare a number of metals and alloys with targeted compositions [4,6–24]. The raw materials used in traditional Fe–Ti production processes are Fe_2O_3 and TiO_2 powders. The results of former studies show that Fe–Ti intermetallic alloys can be prepared from mixed (Fe, Ti) oxide concentrates using the FFC process [4]. A high-purity, and high-opacity Fe–Ti intermetallic alloy consisting of β -Ti (FeTi_4) and FeTi phases can also be prepared from mixed (Fe, Ti) oxide concentrates using this process [4].

To obtain such high-purity Fe–Ti intermetallic alloys, FeTiO_3 and TiO_2 were selected as the raw materials, and used in FeTiO_3 : TiO_2 molar ratios of 2.78:1.00 and 0.58:1.00. At these titanium and iron compositions, FeTi and β -Ti containing iron can co-exist in equilibrium in the temperature range 595–1085 °C, as shown in the Fe–Ti equilibrium phase diagram and mentioned in our earlier research paper [4].

In the present research work, we investigated the direct electrochemical reduction of a mixture of FeTiO_3 and TiO_2 in the above molar ratios. We obtained high purity Fe–Ti equilibrium compositions containing FeTi and β -Ti (FeTi_4) phases after appropriate pellet sintering followed by pre-electrolysis and electrolysis.

2. Experimental

FeTiO_3 (particle size \sim 100 mesh, 99.9% purity, Sigma–Aldrich Group, St. Louis, MO, USA) and TiO_2 (particle size \sim 5 μm , 99% purity, Wako Pure Chemical Industries Ltd., Osaka, Japan) powders were mixed, using a mortar, in FeTiO_3 : TiO_2 molar ratios of 2.78:1.00 or 0.58:1.00, and milled in a planetary mono-mill (Pulverisette 6, FRIETSCH, Idar-Oberstein, Germany) using zirconia balls (diameter 10 mm) at 300 rpm for 1 h, followed by 100 rpm for 1 h. The mixture was then pressed in a hydraulic press into 2.2-g pellets (diameter 15 mm, thickness 4.20–4.95 mm) under a load of 20 MPa for 15 min. The pellets were heated in an infrared gold image furnace (RHL-P410C, ULVAC-RIKO Inc., Yokohama, Japan) to 1000 °C at a constant heating rate of 50 °C/min, and then kept for 2 h under high-grade argon (99.9999% purity) flowing at 100 mL/min, to increase the conductivity and to give sufficient operational strength for connecting to an electrode.

In the electrolysis experiments, molten CaCl_2 was used as the electrolyte. Approximately 380 g of CaCl_2 granules (99% purity, Kojundo Chemical Laboratory Co. Ltd., Saitama, Japan) were placed in a graphite crucible (i.d. 60 mm, o.d. 80 mm, height 150 mm). The graphite crucible was placed in a sealable stainless-steel reactor (i.d. 132 mm, o.d. 140 mm, height 245 mm). All these procedures were performed in a glove box because CaCl_2 is very hygroscopic.

The stainless-steel reactor was then placed in an electric muffle furnace (MIR-4, Irie Shokai Co. Ltd., Tokyo, Japan). After evacuating the stainless-steel reactor, high-grade argon (99.9999% purity) was continuously flowed through the reactor at 100 mL/min. The CaCl_2 was dehydrated at 300 °C for 12 h and 600 °C for 2 h to remove moisture. The temperature was then increased to the experimental temperature of 950 °C. The experimental arrangement of the reactor for electrolysis of the mixed oxide pellets in the molten CaCl_2 bath was shown in our earlier research paper [4].

The temperature was held at 950 °C for 1 h to ensure complete homogenization of the electrolyte before the electrolysis treatment. A stainless-steel rod (diameter 2 mm, length 350 mm), used as the cathode, was then slowly submerged in the electrolyte for pre-electrolysis, with a graphite crucible as the anode, connected by a stainless-steel rod (diameter 2 mm, length 250 mm). Pre-electrolysis of the electrolyte was started to remove the remaining moisture and volatile impurities. The pre-electrolysis was carried out at a voltage of 2.2 V, which is below the theoretical decomposition voltages of CaCl_2 (3.18 V) and CaO (2.63 V) at 950 °C [4].

The pre-electrolysis of the electrolyte was stopped after 8–10 h, when the current was lower than 0.09–0.21 A and the value was stable. The pre-electrolysis cathode was replaced by a mixed FeTiO_3 / TiO_2 pellet attached to a stainless-steel rod. The mixed oxide pellet cathode was slowly submerged in the electrolyte for constant-voltage electrolysis. The cathode was submerged in the electrolyte at the center of the graphite crucible. The submerged position was achieved by lowering the cathode to the bottom of the crucible and then raising it 25 mm. The constant-voltage electrolysis was carried out at a constant voltage of 3.0 V, which is above the theoretical electro-decomposition voltage of CaO and below that of CaCl_2 at 950 °C.

Electrolysis was continued for 25–30 h until the current was lower than 0.75–1.03 A and the value was stable. The electrolysis was controlled using a stabilized power supply (PWR 400L, KIKUSUI, Yokohama, Japan), with simultaneous monitoring of the current–time curve. After termination of the constant-voltage electrolysis, the cathode was removed from the electrolyte and cooled in an argon atmosphere in the upper region of the reactor. The cathode was then removed from the reactor and washed in distilled water, using an ultrasonic bath, to dissolve the solidified salts at the cathode, followed by drying at 100 °C in a vacuum oven.

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