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Fe–Ti ALLOY PRODUCTION FROM MIXED ILMENITE AND TITANIUM DIOXIDE BY DIRECT ELECTROLYTIC REDUCTION IN MOLTEN CALCIUM CHLORIDE ELECTROLYTE

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Abstract

The electrolytic reduction process of mixed ilmenite ($FeTiO_3$) and titanium dioxide (TiO_2) to Fe–Ti intermetallic alloy in molten calcium chloride ($CaCl_2$) electrolyte was studied. $FeTiO_3$ and TiO_2 powders were taken, which was then mixed, milled and pressed into 2.2 g of pellet and heat treated at 1000 °C for 2 h. The pellet was reduced electrochemically in a molten $CaCl_2$ electrolyte at 950 °C and at a constant voltage of 3.0 V. The electrolyzed samples formed by the electrolytic reduction of the mixed $FeTiO_3$ and TiO_2 pellets were analyzed using X-ray diffraction, scanning electron microscopy/energy-dispersive X-ray spectroscopy, electron-probe microanalysis. From this analysis, it was confirmed that the mixed $FeTiO_3$ and TiO_2 pellets were successfully reduced to a dense Fe–Ti intermetallic alloy consisting of β-Ti ($FeTi_4$) and FeTi phases.

1. Introduction

Ilmenite ($FeTiO_3$) is a naturally occurring, abundant and economically important mineral. It is the most important ore of titanium. Most ilmenite ($FeTiO_3$) is mined for titanium dioxide (TiO_2) production. As sources of high grade titanium mineral decreases worldwide, the process involving low grade minerals such as $FeTiO_3$ are given much more importance. However, due to the high content of impurities, especially iron oxides, it is necessary to be refining to obtain titanium rich material or to make ferro-titanium (Fe–Ti) alloy.

Fe–Ti alloy has excellent hydrogen storage ability as well as low expansion rate [1]. So it can be potentially used as a solid hydrogen storage material. Therefore, the preparation of Fe–Ti alloy has become a more challenging research topic. It is also more important to produce Fe–Ti alloy in a more economical process rather than the traditional process. Therefore, we are trying to prepare Fe–Ti intermetallic alloy with the help of electrolytic reduction process as it requires lesser processing steps, low labor requirements, and the ability to reduce a combination of different metal oxides to form alloys.

Since the novel molten salt electrolysis process, namely FFC (Fray, Farthing, and Chen) Cambridge process, was advanced, a number of metals and alloys were prepared successfully by this process [2–12]. In the present study, Fe–Ti intermetallic alloy of dense phase was prepared in the molten $CaCl_2$ electrolyte by using mixed $FeTiO_3$ and TiO_2 pellet as cathode. The constant-voltage electrolysis was carried out at 950 °C and at a voltage of 3.0 V. The phases and microstructure of the electrolyzed pellets were analyzed as well.

2. Experimental procedures

$FeTiO_3$ (particle size ~100 mesh, 99.9% purity, Sigma-Aldrich Group, St. Louis, MO, USA) and TiO_2 (particle size ~5 μm, 99% purity, Wako Pure Chemical Industries Ltd., Osaka, Japan) powders were mixed, using a mortar, in a molar ratio of $FeTiO_3$:TiO_2 = 0.58:1.00, and milled in a planetary mono-mill (Pulverisette 6, FRITSCH, 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 4.95 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 as well as 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 the electrolysis of the mixed oxide pellets in the molten $CaCl_2$ bath has already been shown in our earlier research work [2].

The temperature was held at 950 °C for 1 h to ensure complete homogenization of the electrolyte before the electrolysis treatments. 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 constant 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 [2].

The pre-electrolysis of the electrolyte was stopped after 10 h, when the current was lower than 0.09 A and the value was stable. The pre-electrolysis cathode was replaced by the mixed $FeTiO_3$ and 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 30 h until the current was lower than 0.75 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 on the cathode, followed by drying at 100 °C in a vacuum oven.

After electrolysis, the electrolyzed cathode pellets were visually inspected for color and dimension changes. The conductivities of the cathode pellets were measured by a four-point probe device, used widely for the investigation of electrical phenomena. After measuring the density and electrical conductivity of the electrolyzed cathode, it was cut in a cross-section using a diamond cutter (RCA-005, Refine Tec Ltd., Yokohama, Japan), followed by polishing of the surface and the cross-section. The alloy was then characterized using X-ray diffraction (XRD; Cu Kα; RINT 2200, Rigaku, Tokyo, Japan), scanning electron microscopy (SEM; VE-9800, KEYENCE, Osaka, Japan) with energy-dispersive X-ray spectroscopy (G-XM2, EDAX, Mahwah, NJ, USA), electron-probe microanalysis (EPMA; JXA-8200, JEOL, Tokyo, Japan).

3. Results and discussion

3.1 Heat treatment of mixed $FeTiO_3$ and TiO_2 cathode

Mixture of $FeTiO_3$ and TiO_2 (anatase) pellets with molar ratio of 0.58:1.00, were thermally treated at 1000 °C for 2 h. XRD analysis showed that a mixture of $FeTiO_3$ and TiO_2 (rutile) phases were formed by treatment for 2 h. The SEM micrographs showed that the oxide mixture contained more compact particles of size around 2–10 μm.

This showed that the operational strength of the oxide mixture pellet had been sufficiently increased. It was also found that the conductivities of the above conditioned cathode pellets before thermal treatment were 10^{-6} s/cm. However, the conductivities of the cathodes after thermal treatment increased to 10^{-4} s/cm. **Figure 1** and **Figure 2** shows the XRD patterns and SEM micrographs of the mixed $FeTiO_3$ and TiO_2 powder after milling and thermal treatment under the above conditions.

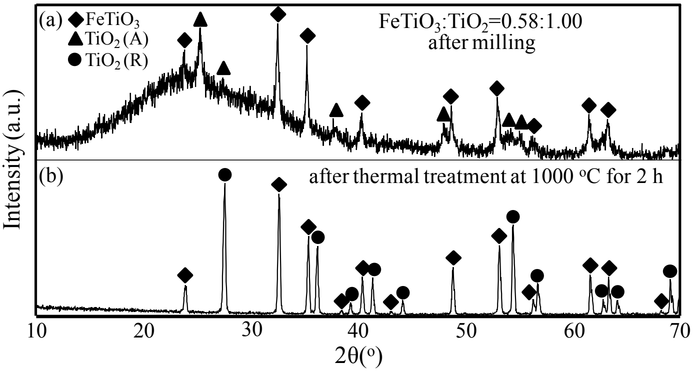

Figure 1 XRD patterns of mixed $FeTiO_3$ and TiO_2 powder (a) after milling, and (b) after thermal treatment at 1000 °C for 2 h

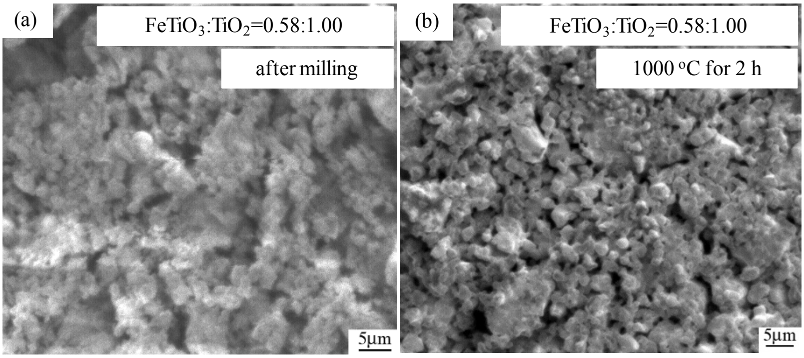

Figure 2 SEM micrographs of mixed $FeTiO_3$ and TiO_2 (a) after milling, and (b) after thermal treatment at 1000 °C for 2 h

3.2 Pre-electrolysis

Pre-electrolysis of the molten $CaCl_2$ electrolyte was carried out at 950 °C and at a voltage of 2.2 V for 10 h, until the current was lower than 0.09 A, to remove the remaining moisture and volatile impurities. A typical current–time plot of the pre-electrolysis is shown in **Figure 3**.

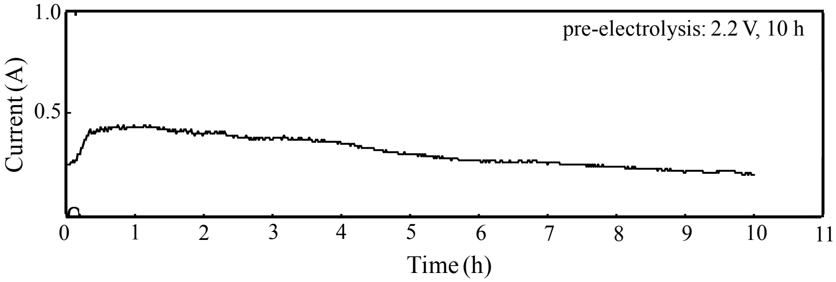

Figure 3 Current–time plot of the pre-electrolysis

Pre-electrolysis developed in four different stages, as shown in **Figure 3**. However, the discussion of each stage of the current–time plot of the pre-electrolysis to remove the remaining moisture has already been discussed in our earlier research work [2].

3.3 Electrolysis

Electrolysis of the mixed $FeTiO_3$ and TiO_2 cathode pellets were carried out at 950 °C and at a constant voltage of 3.0 V for 30 h, until the current was lower than 0.75 A. A typical current–time plot of the electrolysis is shown in **Figure 4**.

Electrolysis developed in five different stages, as shown in **Figure 4**. However, the discussion of each stage of the current–time plot of the electrolysis to convert Fe–Ti intermetallic alloy has already been discussed in our earlier research work [2].

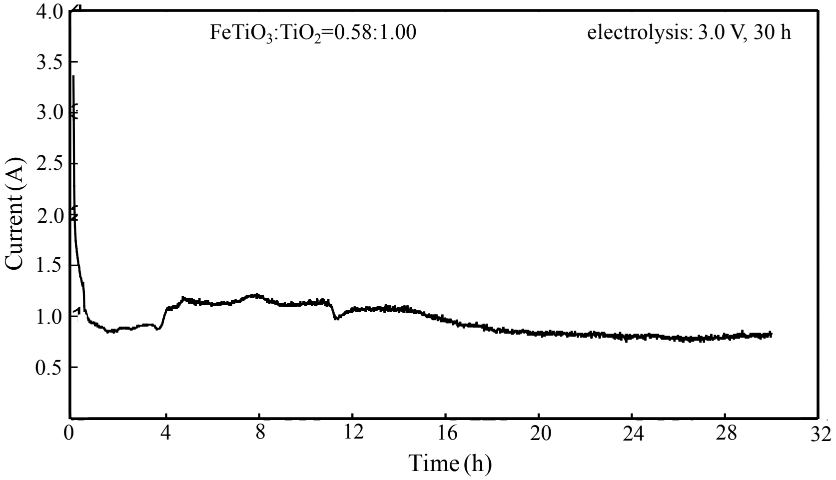

Figure 4 Current–time plot of the electrolysis of mixed $FeTiO_3$ and TiO_2 (0.58:1.00) cathode

The electrolytic reduction of the mixed $FeTiO_3$ and TiO_2 cathode basically occurred in three steps, summarized as follows:

(i) The electrically semiconducting mixed $FeTiO_3$ and TiO_2 cathode was converted to a highly conducting phase with the removal of a small amount of oxygen. Continuous electrolysis removed oxygen from the cathode by electrochemical dissociation. The dissociated oxygen dissolved in the electrolyte, and was then removed as CO or CO_2 at the anode, leaving a Fe–Ti intermetallic alloy such as FeTi at the cathode. The possible cathode reaction is as follows:

$$FeTiO_3(s) + 2e^- = Fe(s) + TiO_2(s) + O^{2-} \quad (1)$$

$$Fe(s) + TiO_2(s) + 4e^- = FeTi(s) + 2O^{2-} \quad (2)$$

$$2TiO_2(s) + 4e^- = Ti_2O_3(s) + 2O^{2-} \quad (3)$$

$$Ti_2O_3(s) + 2e^- = 2TiO(s) + O^{2-} \quad (4)$$

$$TiO(s) + 2e^- = Ti(s) + O^{2-} \quad (5)$$

$$Fe(s) + TiO(s) + 2e^- = FeTi(s) + O^{2-} \quad (6)$$

(ii) As a result of the high solubility of oxygen ions, the electrolyte contained some CaO. The ionization of CaO in the molten electrolyte is as follows:

$$\mathrm{CaO\ (in\ CaCl_2) = Ca^{2+} + O^{2-}} \tag{7}$$

The calcium cations were reduced to metallic calcium, which was deposited on the cathode surface. The calcium reacted with the mixed $FeTiO_3$ and TiO_2 cathode to form the Fe–Ti intermetallic alloy:

$$\mathrm{Ca^{2+} + 2e^{-} = Ca(l)} \tag{8}$$
$$\mathrm{FeTiO_3(s) + Ca(l) = Fe(s) + CaTiO_3(s)} \tag{9}$$
$$\mathrm{Fe(s) + CaTiO_3(s) = FeTi(s) + Ca^{2+} + 3O^{2-}} \tag{10}$$
$$\mathrm{TiO_2(s) + Ca^{2+} + O^{2-} = CaTiO_3(s)} \tag{11}$$
$$\mathrm{TiO_2(s) + 2Ca(l) = Ti(s) + 2CaO(s)} \tag{12}$$

(iii) The oxygen ions dissolved in the electrolyte were discharged at the graphite anode and reacted with carbon to form CO and CO_2 gases:

$$\mathrm{O^{2-} + C(s) = CO(g) + 2e^{-}} \tag{13}$$
$$\mathrm{2O^{2-} + C(s) = CO_2(g) + 4e^{-}} \tag{14}$$

The mechanism of the electrolysis i.e., electrolytic reduction and the calcium reduction of the mixed oxide cathode to a Fe–Ti intermetallic alloy was shown in our earlier research work [2].

After electrolysis for 30 h, the electrolyzed cathode pellets were visually inspected for color and dimension changes. The conductivities of the cathode pellets were measured and it was found that the conductivities of the mixed $FeTiO_3$ and TiO_2 cathode pellets before electrolysis were 10^{-4} S/cm. However, the conductivity of the above cathode pellets after electrolysis increased to 10^{3} S/cm, which showed metallization of the cathode. After measuring the conductivities of the cathode pellets, they were cut into cross-sectional pieces, using a diamond cutter, for instrumental analysis.

Figure 5 shows the SEM back-scattering micrographs of the surface and cross-section of the mixed $FeTiO_3$ and TiO_2 electrolyzed cathode of composition 0.58:1.00. The chemical structures of the cathode phases after electrolysis were determined by quantitative analysis using EPMA. From **Figure 5**, it is clearly seen that FeTi intermetallic phases of size around 5–10 μm were dispersed in a matrix of a β-Ti phase of chemical composition $FeTi_4$. The β-Ti phase is in the form of a $Fe_{1-x}Ti_x$ metastable alloy, where x is less than 0.8 [2, 13]. It was obvious that the alloy structure with β-Ti ($FeTi_4$) and FeTi intermetallic phases was quite dense and without pores, as shown in **Figure 5**. **Figure 6** shows the XRD patterns of the surface and cross-section of the mixed $FeTiO_3$ and TiO_2 electrolyzed cathode of composition 0.58:1.00. The XRD and SEM back-scattering analysis shows that the surface and the cross-section of the cathode were converted to β-Ti ($FeTi_4$) and FeTi intermetallic phases. **Figure 7** shows the EPMA mapping of the surface of the mixed $FeTiO_3$ and TiO_2 electrolyzed cathode of composition 0.58:1.00.

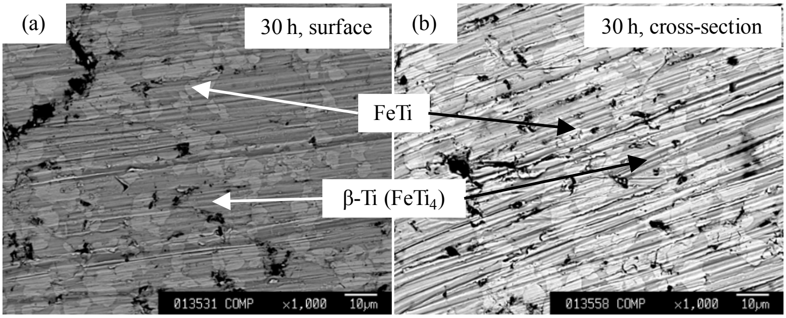

Figure 5 SEM back-scattering micrographs of the mixed $FeTiO_3$ and TiO_2 (0.58:1.00) cathode pellets (surface and cross-section) electrolyzed for 30 h

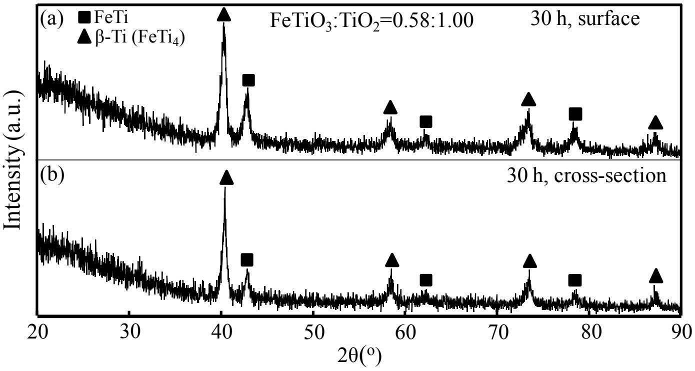

Figure 6 XRD patterns of the mixed $FeTiO_3$ and TiO_2 (0.58:1.00) cathode pellets (surface and cross-section) electrolyzed for 30 h

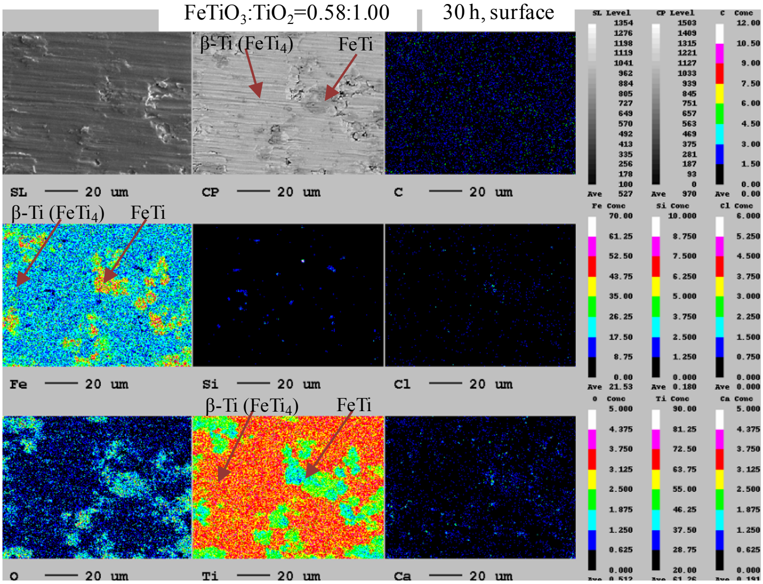

Figure 7 EPMA mapping of the mixed $FeTiO_3$ and TiO_2 (0.58:1.00) cathode pellets (surface) electrolyzed for 30 h

In this research work, it was found that β-Ti ($FeTi_4$) and FeTi were the major phases in the surface as well as the cross-section of the mixed $FeTiO_3$ and TiO_2 cathode after electrolysis. The β-Ti ($FeTi_4$) phase formed was a single body-centered cubic phase, which equilibrates with the FeTi phase, as per the Fe–Ti equilibrium phase diagram.

4. Conclusion

Production of Fe–Ti intermetallic alloy, based on the FFC process, was investigated in this research work. Mixed and sintered $FeTiO_3$ and TiO_2 pellets in a molar ratio of 0.58:1.00 pellets were electrolyzed in a molten $CaCl_2$ electrolyte at 950 °C with a constant voltage of 3.0 V after pre-electrolysis to remove moisture and impurities from the electrolyte. The cathode pellets of composition 0.58:1.00 was successfully reduced to a dense Fe–Ti intermetallic alloy of FeTi and β-Ti ($FeTi_4$) phases. FeTi phases of size around 5–10 μm were dispersed in a matrix of the β-Ti ($FeTi_4$) phase.

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