Electroplating of titanium on iron by galvanic contact deposition in NaCl–TiCl₂ molten salt

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Abstract

A commercial titanium coating method is not available with the exception of physical vapor deposition or titanium cladding which are very expensive processes. However, it is very attractive to coat the surface of steel with a thin titanium layer for improving its corrosion resistance against salt water or acids. This paper describes a method for electroplating a thin titanium layer on an iron surface by galvanic contact deposition in which pure titanium and an iron electrode are immersed into a molten salt (NaCl–TiCl₂) at high temperature; both electrodes are connected through an external circuit. By immersing iron in the molten salt for 10 h at 1200 K, we obtained a flat and thin layer of titanium–iron alloy on iron. The thickness and composition of this layer were 50 ± 10 μm and Ti—15–16 mol% Fe, respectively. The corrosion resistance of this titanium-rich alloy layer is expected to be greater than that of steel. Galvanic contact deposition is a very simple method in which iron and titanium electrodes are just immersed into molten salts without the use of an external power source. Thus, the capability of the method presently proposed could be suggested so as to improve the corrosion resistance of steel, particularly from the practical process point of view.

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1. Introduction

Metallic titanium exhibits excellent corrosion resistance against salt water, hydrogen chloride, etc. Therefore, titanium metal is used in desalination and chemical plants and occasionally used in the construction of roofs for baseball stadium, etc. Titanium ore (titanium oxide) is available in abundance and the process of its conversion to chloride is well established. However, the reduction of titanium tetrachloride to metallic titanium is known to be an expensive process. For this reason, it is very attractive to develop a method for electroplating titanium on base structural materials such as iron.

The redox potential of titanium and titanium ion equilibrium is considerably less noble than the reduction potential of water. Thus, molten salts of alkaline or alkaline earth halides are used as a solvent in the electrolysis for titanium. In general, the electrolysis of titanium in a molten salt at high temperature produces titanium in the form of a sponge or dendrite. However, its morphology is unsuitable for a layer with high corrosion resistance. Titanium layers without sponge and dendrite forms have been successfully obtained by several groups after many trials [1–7]. They significantly decreased the deposition current in order to prevent it from reaching the level of the diffusion limiting current. Alternatively, Straumanis et al. [8], Steinman et al. [9], Oki and Choh [10], and Muro et al. [11] utilized a disproportionation reaction of Ti²⁺ to metallic titanium and Ti³⁺ on iron in molten salts at high temperatures and produced smooth and flat titanium layers on the iron surface.

The purpose of this paper is to present an electroplating technique that involves galvanic contact deposition of...
titanium in a molten salt of NaCl–TiCl₂ based on the experimental results previously reported by the present authors [12] with additional experimental results and discussion. In this study, TiCl₂ is used as a titanium ion source because TiCl₄ is volatile and the solubility of TiCl₄ into molten NaCl is small, and TiCl₂ is easier to be treated than TiCl₃.

2. Galvanic contact deposition

The phase diagram of Fe–Ti system is shown in Fig. 1 [13]. It indicates that the solubility of iron in αTi (HCP structure, low-temperature phase) is low, while that in βTi (BCC, high-temperature phase) is relatively high, more than 20 mol% Fe. It should be noted that two intermetallic compounds FeTi and Fe₂Ti exist in this system. In Fig. 2, the calculated activity of titanium at 1173 K using parameters fitted by CALPHAD [14] is plotted as a function of mol fraction of Ti in Fe–Ti alloy. Fig. 3 shows a conceptual diagram of the galvanic contact deposition method employed in this work. As shown in this figure, we immersed titanium and iron electrodes into a molten salt that contains Ti²⁺; the electrodes were connected through an external circuit. A difference in the titanium activity (see Fig. 2) at the two electrodes leads to anodic dissolution of titanium from the titanium electrode and cathodic deposition of titanium on the iron electrode. Electrons and titanium ions can migrate through the external circuit and molten salt, respectively. These reactions can be written as follows:

- titanium anode:
  \[ \text{Ti} \rightarrow \text{Ti}^{2+} + 2\text{e}^-; \]  
  (1)

- iron cathode:
  \[ \text{Ti}^{2+} \text{on Fe} + 2\text{e}^- \rightarrow \text{Ti} + \text{Fe alloy}; \]  
  (2)

3. Experimental

The schematic diagram of the apparatus used in this work is shown in Fig. 4. The experimental conditions are summarized in Table 1. A titanium crucible was used as the anode (titanium electrode). Lumps of sponge titanium were placed at the bottom of the crucible in order to increase the anode surface area. One or two iron electrodes were immersed in the molten salt and attached to stainless steel tubes. The iron electrode was connected to the anode through an external circuit. The areas of immersed iron electrode were 4.12 cm² for exp. #1 and 10.50 cm² for exp. #2A and #2B. When the two iron electrodes were immersed (exp. #2), one of them was connected to the anode forming a closed circuit, while the other was not connected, and kept in an open circuit. In addition, a titanium rod was immersed into the molten salt as a reference electrode (exp. #2). Each electrode comprised iron/titanium immersed in the molten salt, a potential lead (iron wire), and a stainless steel tube, where the tube was used as a current lead. The iron wire was used as the potential lead to minimize the effect of thermal electromotive force on the measurement of open circuit voltage. The
external current was monitored by a voltage drop across a standard resistance of 1 mΩ (shunt resistance). The temperature was maintained at 1173 K (or 1200 K) in an argon atmosphere. NaCl-1 mass % (0.49 mol%) TiCl2 was used as the molten salt. It should be noted that the concentration of TiCl2 was significantly less than its solubility in molten NaCl (the solubility was reported to be ~42 mol% at 1073 K [15]). TiCl2 was synthesized by a method described in our previous report [16]. After the experimental apparatus was set up, the atmosphere was replaced with argon gas, and the temperature was increased to 1173 or 1200 K and maintained for 5 or 10 h. The iron electrode was immersed into the molten salt after the temperature reached the aimed value and stabilized. We define the reaction time to be zero when the iron electrodes were immersed into the molten salt. After immersion for 5 or 10 h, they were pulled above the molten salt, and the reaction chamber was cooled.

4. Result and discussion

4.1. Open circuit voltages and external currents

Fig. 5 shows the variation of the external current and the electric charge passed through the external circuit measured in exp. #1. The initial external current was ~4 mA/cm², and it decreased gradually to ~2.5 mA/cm² after 10 h. A total electric charge of 104 C/cm² (normalized by the surface area of the iron electrode immersed into the molten salt) was passed through the external circuit. In this experiment, the external circuit was opened several times to measure the open circuit voltage between the iron and titanium electrodes. Fig. 6(A) shows the change of voltage between anode and cathode in exp. #1 (1200 K). As shown in this figure, a relatively large value (120 mV) of the open circuit voltage was detected initially, while it rapidly decreased below 10 mV and was 4.5 mV after 10 h. The titanium reference electrode was used in exp. #2A and #2B (1173 K), and the potentials of the titanium electrode (i.e. titanium crucible) and iron electrodes under open (exp. #2A) and closed circuits (exp. #2A) were measured against the reference electrode. The results are shown in Fig. 6(B). Initially, the potentials of the iron electrodes against the reference electrode were 90 and 100 mV, respectively. The decrease in potential of the iron electrode in the closed circuit was faster than that of the electrode in the open circuit (it is noted that the titanium deposition on the iron electrode is also expected even in an open circuit condition by a disproportionation reaction mechanism; see Section 4.3 for a detailed discussion). But the deposition rate of titanium on the iron electrode in the open circuit was expected to be less than that in the closed circuit.

4.2. Analysis of deposited layer

Fig. 7 shows a photograph of the iron electrode after the immersion in the molten salt (exp. #2A). The immersed

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**Table 1**

Summary of the experimental conditions in this work

| Exp. no. | Temperature (T/K) | Immersion time (t/h) | External circuit | Immersed area of iron rod (A/cm²) | Concentration of TiCl₂, mol% of TiCl₂ |
|----------|-------------------|----------------------|------------------|----------------------------------|-------------------------------------|
| 1        | 1200              | 10                   | Closed           | 4.12                             | 0.49                                |
| 2A       | 1173              | 5                    | Closed           | 10.50                            | 0.49                                |
| 2B       | 1173              | 5                    | Open             | 10.50                            | 0.49                                |

0.49 mol% of TiCl₂ equals 1 mass % of TiCl₂ or 0.4 mass % of Ti²⁺ in NaCl-TiCl₂ molten salt.
part exhibits a shiny metallic silver color. Figs. 8 and 9 show EPMA (electron probe micro-analysis) photographs of the cross section and surface of the iron electrode, respectively. The thickness of the deposit layer was \(50 \pm 10\,\mu m\). The composition of this titanium-rich layer on the surface was confirmed to be Ti—15–16 mol\%\,Fe by the line composition analysis of the cross section (Fig. 8) and point analysis of the surface (Fig. 9). In addition, an X-ray diffraction (XRD) pattern of the surface confirmed that the deposit layer has a BCC structure (the XRD pattern is not provided in this report). Thus, we assume that the surface layer is the \(\beta\)Ti phase (high-temperature phase). In the microphotograph of the cross section, an additional layer was observed between the \(\beta\)Ti and \(\alpha\)Fe phases. The EPMA analysis suggests that this thin layer could be an intermetallic compound, FeTi phase, as expected from the Fe–Ti phase diagram. Although the presence of another intermetallic phase, Fe\(_2\)Ti, is expected, it could not be observed in this study. As shown in Figs. 8 and 9, the surface of deposit layer on the iron electrode was relatively smooth and flat. Its weight gain after the experiment was 24.4 mg/cm\(^2\), which corresponded to the \(\beta\)Ti layer with a thickness of 56\,\mu m from the calculation, under the assumption that the density of the deposited alloy layer was equal to that of pure \(\beta\)Ti \((\rho = 4.4\,g/cm^3)\). Moreover, the electric charge of 104 C/cm\(^2\) monitored in the external circuit was equivalent to the thickness of 59\,\mu m of pure titanium. These values are in good agreement with the thickness \((50 \pm 10\,\mu m)\) estimated from the EPMA analysis within the experimental error. These results are consistent with the reactions of Eqs. (1) and (2) predicted.

The open circuit voltage measured after 10 h was 4.5 mV; it corresponds to the activity of titanium \((a_{Ti})\) of 0.92. According to Fig. 2, the titanium activity of 0.92 equals \(x_{Ti} = 0.93\) [14]. However, the composition of the surface determined by EPMA were in the range of 0.84–0.85. Thus, there is a small difference between the EPMA result and the value expected from the measurement of the open circuit voltage. On the other hand, the potential of the titanium-iron electrode at \(x_{Ti} = 0.84\) is calculated to be
15 mV against the titanium electrode. Therefore, the observation (4.5 mV) and calculation differs by about 10 mV. This difference could be attributed to the following reason. The disproportionation reaction, which is proceeding even in open circuit condition, might reduce the open circuit voltage. In addition to this, such small voltage was possibly affected by unexpected factors such as a fluctuation in the concentration of titanium ions and/or the thermal electromotive force due to nonuniform temperatures in the crucible.

4.3. Comparison between short and open circuit experiments

The weight gain of the iron electrode under the closed circuit condition is compared with that under the open circuit condition (exp. #2A and 2B, respectively, at 1173 K for 5 h). It was 3.29 mg/cm² in the closed circuit and 1.27 mg/cm² in the open circuit. The deposition of titanium under the open circuit condition is probably based on a disproportionation reaction [8–11]. The reaction mechanism is illustrated in Fig. 10. The concentration of Ti³⁺ ions in the vicinity of each electrode is different due to the difference in the titanium activity at the electrodes; the concentration Ti³⁺ ions is regulated by

\[ K = \frac{a_{Ti}^2a_{Ti^3+}}{a_{Ti^3+}} \]

where \( K \) represents the equilibrium constant of the disproportionation reaction of Ti²⁺ to Ti and Ti³⁺ and \( a_i \) denotes the activity of each substance. It is evident from Eq. (3) that the equilibrium concentration of Ti³⁺ ions at the surface of the iron electrode \((a_{Ti} < 1)\) is greater than that at the titanium electrode \((a_{Ti} = 1)\). Therefore, Ti³⁺ ions migrate from the iron electrode to the titanium electrode, and they are subsequently reduced to Ti²⁺ by titanium metal. However, the concentration of Ti³⁺ ions is small at equilibrium. Thus, the reaction rate of this mechanism may be limited by the diffusion of Ti³⁺. The rate is less than that of the galvanic contact mechanism by which electrons are transferred through the external circuit with the diffusion of abundant Ti²⁺ ions (Eqs. (1) and (2)). In fact, the amount of titanium deposited at 1173 K for 5 h (exp. #2A, open circuit) was less than that deposited at 1173 K for 5 h (exp. #2A, closed circuit).

The amount of titanium deposited at 1173 K for 5 h (exp. #2A, closed circuit) was considerably less than that deposited at 1200 K for 10 h (exp. #1, closed circuit; the deposited amount was 24.4 mg/cm²). It can be inferred that the higher temperature and longer immersion time make an increase of amount of the titanium deposition possible. However, the authors also take the view that no quantitative discussion is given at the present time.

5. Summary

An attempt has been made to propose an electroplating method for producing a titanium–iron alloy layer on the iron surface by the galvanic contact deposition at 1173 or 1200 K for 5 or 10 h. The layer obtained at 1200 K for 10 h was relatively smooth and flat with a thickness of 50 ± 10 μm and the composition of Ti—15–16 mol% Fe. As the results reported in literature, we confirmed the deposition of titanium based on the disproportionation reaction of Ti²⁺. However, the deposition rate of the galvanic contact method was greater than the disproportionation reaction case.

For electroplating a flat layer, the deposition current is required to be less than the diffusion limiting current. Thus, electrode potential must be controlled at very small polarization from the equilibrium electrode potential. However, it is difficult to control the potential of an electrode immersed in molten salt at high temperature. The galvanic contact method employed in this work might be the simpler method for making the electrode potential slightly cathodic against the potential of titanium deposition. Evidently, pure titanium on the iron surface could not be obtained by this method. On the other hand, the 84–85 mol% titanium-rich layer obtained by the present method might be sufficient for improving the corrosion resistance of iron. We believe that the present method is one way to apply for electroplating titanium on the iron surface.

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