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Production of Nb–Ti–Ni alloy in molten $CaCl_2$

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ABSTRACT

A Nb–Ti–Ni hydrogen permeable alloy was synthesized as a powder using the OS process, which involves the simultaneous reduction of a mixture of Nb, Ti, and Ni oxides by Ca that is generated from molten $CaCl_2$ via electrolysis. The mechanism confirmed that a BCC-(Nb, Ti) phase easily formed at an early stage of the reaction followed by the generation of a B2-TiNi phase from the lower oxides such as NbO and Ti_2O. The oxygen content of the synthesized alloy decreased significantly to 0.27 mass% with increased electric charge. The three elements were uniformly distributed at the macroscopic level.

1. Introduction

Alloys that are selectively hydrogen-permeable are useful for clean energy because they can be applied to membrane reactor technology, which separates hydrogen from residual gas mixtures of CH_4 and H_2O [1,2]. For this application, the hydrogen permeability must be high even at low temperatures. Pd–Ag alloy is the main candidate for this application, but it is brittle and expensive and thus undesirable for use in large quantities [1,2].

As an alternative to Pd–Ag alloy, Aoki and co-workers [3–5] developed a Nb–Ti–Ni alloy because its components are relatively cheap and its hydrogen permeability is equal to that of Pd–Ag alloy. Nb–Ti–Ni alloy is generally produced from the corresponding pure metals via arc melting in an inert gas atmosphere. Aoki and co-workers [3–5] reported that this alloy consists of two phases: BCC and B2 solid solutions. This feature contributes to its ductility and good hydrogen permeability [3,4].

Individual refining of metals from their corresponding oxides and subsequent melting to produce the alloy ingots consume a large amount of energy, which increases the price of Nb–Ti–Ni alloy. Nb–Ti–Ni alloy is ductile and flexible when the oxygen content is low, which is favorable for mechanical deformation. Herein, we propose a new production method for Nb–Ti–Ni alloy to decrease the manufacturing costs and achieve low oxygen content.

OS process [6–8] is promising as a method for the preparation of this alloy because it could result in an alloy with low oxygen content that is obtained directly from the oxide mixtures [9,10]. The original idea of the OS process was to remove oxygen from pure oxides using CaO electrolysis in molten $CaCl_2$. Many metals such as pure titanium and nickel have been reduced using this method [6–8]. Accordingly, in this study, we expect to generate Nb–Ti–Ni alloy directly from the corresponding mixture of oxides. Using the same $CaCl_2$ molten salt, Fray and co-workers [11,12] reported the dissolution of oxygen ions from oxides and oxide mixtures to form the corresponding metals and alloys, respectively.

Eqs. (1)–(8) show the expected processes in the formation of the ternary Nb–Ti–Ni alloy.

$$CaO = Ca^{2+} + O^{2-} \quad (1)$$

$$Ca^{2+} + 2e^- = Ca\,(\text{at cathode}) \quad (2)$$

$$nO^{2-} + C = CO_n + 2ne^-\ (n = 1 \text{ or } 2)\,(\text{at anode}) \quad (3)$$

$$Nb_2O_5 + 5Ca = 2Nb + 5CaO\,(\text{reduction}) \quad (4)$$

$$TiO_2 + 2Ca = Ti + 2CaO\,(\text{reduction}) \quad (5)$$

$$NiO + Ca = Ni + CaO\,(\text{reduction}) \quad (6)$$

$$Nb + Ti + Ni = Nb\text{–}Ti\text{–}Ni\ \text{alloy} \quad (7)$$

$$O\,(\text{in Ti}) + Ca = CaO\,(\text{deoxidation}) \quad (8)$$

CaO dissolves to Ca^{2+} and O^{2-} in molten $CaCl_2$, as shown in Eq. (1). Ca^{2+} then undergoes electrolysis to form Ca at the cathode. This Ca metal has a strong reducing ability and thus decomposes other oxides such as Nb_2O_5, TiO_2, and NiO [6–8,13,14]. The generated O^{2-} is transferred to the consumable carbon anode and removed as CO or CO_2 gas bubbles, as shown in Eq. (3). The oxides are reduced by calciothermic reactions, as shown in Eqs. (4)–(6). Because of the

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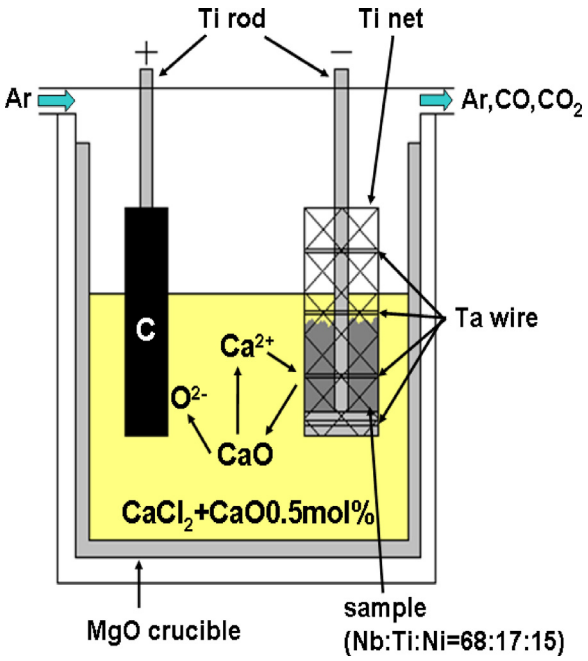

Fig. 1. Experimental apparatus for electrolysis.

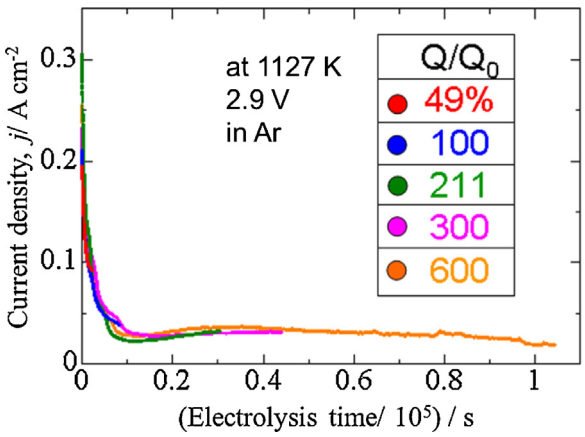

Fig. 2. Change of anodic current density with electrolysis duration.

solubility of Ca in the molten salt, pure Ca does not precipitate on the cathode; the dissolved Ca holds still high reducibility against the oxides. The reduced elemental metals react to form the desired ternary alloy in molten $CaCl_2$, as shown in Eq. (7). The residual oxygen in the alloy is removed via a reaction with Ca to form CaO (Eq. (8)) [6,7,13]. The CaO byproduct dissolves in the molten $CaCl_2$, as shown in Eq. (1). Therefore, the above-mentioned processes in the OS mechanism can continuously repeat without the addition of any new reducing material, which leads to cost-saving. The pure oxides were independently studied via their calciothermic reductions [6–8,14]. It has been reported that TiO_2, which is the most thermodynamically stable oxide, could be successfully reduced to metallic Ti powder with a low oxygen content [6–8]. Descallar et al. [14] reported recently that NiO was reduced by Ca dissolved in a $CaCl_2$ bath via the electrolysis of CaO. It is natural that the calciothermic reaction involving pure Ca proceeds rapidly [13,15], while electrolyzed Ca is sufficiently reactive to remove oxygen from TiO_2 [6–8]. To study the possibility of the synthesis of alloys from oxides, many alloys, including Ti–V [16], Ti–V–Al [9], and Ti–Zr–Ta–Nb [10], have been studied by the present authors.

In this study, we aim to experimentally verify the possibility of applying the OS process for the synthesis of a Nb–Ti–Ni alloy.

2. Experimental

Nb_2O_5, TiO_2, and NiO powders (99.9% purity, <1 μm particle size) were used as starting materials. The appropriate amounts of each powder were weighed to achieve the target composition (68 mol% Nb–17 mol% Ti–15 mol% Ni [3]) and then mixed for over 10 min in an agate mortar. Fig. 1 shows the experimental apparatus used for reduction and electrolysis. $CaCl_2$ (>95%, main impurity is water) and CaO (99.9%) were mixed at a composition of 99.5 mol% $CaCl_2$ and 0.5 mol% CaO and filled into a MgO crucible (90 mm inner diameter, 200 mm deep). A graphite anode rod (10 mm in diameter), basket-shaped cathode (Ti net with 100 mesh), and thermocouple were placed at the top of the crucible. The mixed oxide powder (>2.00 g) was then filled into the titanium basket. The apparatus was slowly heated to 873 K under vacuum and held at that temperature for at least 10 h to remove the water from the vessel. The vessel was then charged with argon gas and the temperature was gradually increased to 1173 K and allowed to stabilize. The electrodes were submerged in the molten salt. A constant voltage of 2.9 V was applied between the electrodes, and the resultant current was recorded at 5 s intervals. After the desired period of electrolysis, the current supply was terminated and the electrodes were raised to the upper part of the vessel. After cooling, the cathode was washed with distilled water. The sample was removed from the Ti cathode and carefully sliced into three parts (i.e., outside, middle, and inside). These three specimens were then separately crushed into finer particles. In order to completely remove the solidified salt residue, the specimens were washed with distilled water, acetic acid, distilled water, ethanol, and acetone in this order. The resultant powder specimens were then dried in vacuum.

The phases were examined using X-ray diffraction (XRD) analysis. The residual oxygen content was determined via an inert-gas-fusion infrared-absorption method using an LECO TC600 oxygen/nitrogen analyzer. The morphologies of the resulting powders were observed using scanning electron microscopy (SEM).

3. Results and discussion

3.1. Current and oxygen concentration

Fig. 2 shows the current density as a function of electrolysis time at 1127 K. Q_0 is the theoretical amount of electricity required to completely reduce the oxides, while Q represents the actual quantity of electricity supplied; therefore, Q/Q_0 indicates the degree of oxygen removal. The anodic current density decreases rapidly within ~10 ks and then continues to decrease more gradually. As shown in Fig. 2, all the samples showed similar current behavior, although some variations in the current were evident. The anodic surface area was evaluated for anodic current density using the trace of the molten salt level on the surface of the carbon rod.

The concentration of oxygen in each of the three parts of the obtained sample (i.e., the outside, middle, and inside of the basket-shaped cathode) was determined (Fig. 3). The oxygen concentration significantly decreased until a Q/Q_0 of 200% was reached and finally decreased to 0.27 mass% at a Q/Q_0 of 600%. In general, the oxygen content was lowest in the part closest to the cathodic surface; this is because the cathodic surface is in frequent contact with the Ca that forms on the net of the Ti basket. Figs. 2 and 3 show that the reduction from the oxides proceeds in a shorter time (Q/Q_0 < 200%), and that deoxidation gradually occurred after reduction.