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New method for low temperature fabrication of Ni–Al alloy powder for molten carbonate fuel cell applications

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ABSTRACT

Lump-free Ni-5 wt% Al alloy powder was successfully prepared using an $AlCl_3$ activator at 400 °C under vacuum. The $AlCl_3$ activator served as the catalyst, lowering the fabrication temperature by 1000 °C compared with the temperature required for the conventional process. The Ni–Al alloy was formed by the following steps: the formation of NiAl by the reaction of the Ni surface with $AlCl_2$ or AlCl produced by the reaction between Al and $AlCl_3$, the formation of Ni_3Al by Al diffusion and reaction, and the formation of a Ni–Al solid solution by Al diffusion into the Ni matrix until the solubility limitation was reached. Although lowering the alloying temperature lengthens the reaction time, the time could be reduced by controlling the amount of $AlCl_3$. A single cell test and a creep test were also conducted using a green sheet of as-prepared Ni–Al alloy powder as an anode of a molten carbonate fuel cell (MCFC).

Introduction

Ni–Al alloys are widely used for several applications, such as in automobile engines, aircraft construction, and electricity generation and energy conversion equipment, because of their high melting points, relatively low density, good strength and high corrosion and oxidation resistance [1–3]. In particular, Ni–Al alloy powder has been intensively used as an anode material for molten carbonate fuel cells (MCFCs), one of the most promising power generation systems due to their high energy conversion efficiency, low emissions and flexible fuel utilization [4,5]. Because the Ni–Al alloy has sufficient creep resistance and appropriate electrical conductivity and catalytic activity, it is suitable as an anode material for MCFCs [6–8]. If an anode material has poor creep resistance, then creep and sintering problems lead to the collapse of the pore structure of the anode, resulting in an increase in irreversibility, degradation of cell performance and shorter operation time. Although the Ni–Al alloy is a suitable anode material for MCFCs, its high fabrication cost has become an obstacle to the commercialization of MCFCs. The general method of preparation of the Ni–Al alloy requires a high temperature of approximately 1400 °C to melt nickel and aluminum to make a

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solid solution, as well as a pure H_2 atmosphere to prevent the oxidation of Ni and Al. This high temperature process sharply increases the cost of fabrication of the Ni–Al alloy material [9,10]. Moreover, because powder is melted and sintered at high temperature during the Ni–Al alloying process, large Ni–Al alloy lumps are obtained. Thus, after the Ni–Al alloy is produced, a pulverization process is required to obtain powder with a suitable particle size, which influences the supply of reactant gas to the electrochemical reaction sites because particle size and shape determine the pore structure of the MCFC electrode, i.e., its pore size and porosity. The requirement for a pulverization process after the fabrication of the Ni–Al alloy also contributes to the high price of Ni–Al powder. Thus, from the point of view of reducing the cost of fabrication, low temperature synthesis of Ni–Al alloy powder without agglomeration between particles is highly attractive.

Our group has already proposed a new low temperature process for the fabrication of Ni–Al alloy powder [11]. This method uses $AlCl_3$ vapor as an activator of the chemical reaction between Ni and Al in a pure H_2 atmosphere, enabling the temperature for the fabrication of the Ni–Al alloy to be decreased to 700 °C. At 700 °C, $AlCl_3$ vapor continues to flow with pure H_2 gas into the furnace with the mixture of nickel and aluminum. The Ni–Al alloy powder forms at low temperature according to the following chemical reaction process:

$$AlCl_3(g) + Al(s) \rightarrow AlCl(g) + AlCl_2(g) \quad (1)$$

$$AlCl(g) + AlCl_2(g) + Ni(s) \rightarrow Ni - Al(s) + AlCl_3(g) \quad (2)$$

As seen in the above equations, $AlCl_3$ initiates the reaction between nickel and aluminum. First, $AlCl_3$ reacts with Al, producing the activated forms of AlCl or $AlCl_2$. These species then react with nickel and form Ni–Al deposits on the nickel surface. Al atoms on the surface of nickel diffuse into the inner portions of nickel particles, and AlCl and $AlCl_2$ return to $AlCl_3$. Finally, the Ni–Al alloy powder is produced at low temperature.

Although this method can dramatically reduce the fabrication temperature of the Ni–Al alloy, it still requires a pulverization process to reduce the particle size because large Ni–Al alloy lumps are obtained after the heat treatment. Another problem with this process is that it is difficult to keep the $AlCl_3$ vapor and H_2 gas flowing until alloying is complete. As $AlCl_3$ is highly corrosive, components such as the pipe lines and furnaces can become severely corroded. Expensive pure H_2 gas also has to be flowed during the heat treatment, and this is one of the factors leading to a high fabrication cost.

This paper reports our attempts to modify this method to solve the various problems mentioned above. To reduce the amount of $AlCl_3$ and to avoid using H_2 gas, an ampule-type reactor maintained under vacuum was designed for the fabrication of Ni–Al alloy powder from a mixture of nickel and aluminum elemental powders. As shown in the chemical reaction Equations of (1) and (2), $AlCl_3$ acts as the catalyst for this reaction. Thus, it is necessary neither to use a large amount of $AlCl_3$ nor to introduce pure H_2 gas flowed into the furnace to prevent the oxidation of nickel and aluminum before the chemical reaction between nickel and aluminum is complete. In this study, we try to solve the oxidation problem by maintaining vacuum. Additionally, the pulverization process can be removed by reducing the reaction temperature to 400 °C.

In this study, we have prepared Ni–Al alloy powders from a mixture of Ni and Al elemental powders at low temperature under vacuum, using a small amount of $AlCl_3$ as an activator and without using pure H_2. The effects of reaction temperature and the amount of $AlCl_3$ catalyst on alloy formation have been investigated.

Experimental

Fabrication of Ni–Al alloy powder

Ni–Al alloy powder was prepared according to the following process. Powders of jagged and chain-shaped nickel (Inco 255, VALEINCO, Inc.) with an average particle size of 4.0 μm, spherical-shaped aluminum (Alfa Aesar) with a size of 4.2 μm and $AlCl_3$ (99%, Junsei) were placed into a quartz ampule. The quartz ampule containing Ni, Al and $AlCl_3$ was sealed after reaching 10^{-4} Torr vacuum using a diffusion pump. The Al content was maintained at 5 wt% because Ni-5 wt% Al alloy has generally been used for MCFC anode materials [6–8]. The as-sealed quartz ampule with reactants was heated up inside a furnace to a desired reaction temperature between 300 and 600 °C. After the reaction, the reactor was slowly cooled down to room temperature. The procedure for the preparation of Ni–Al alloy powder is presented in Fig. 1.

The phases and morphologies of as-prepared Ni–Al alloy powder were characterized by an X-ray powder diffractometer (XRD, Rint/DMAX 2500-Rigaku) and a field emission scanning electron microscope (FE-SEM, NOVA NanoSEM200). The particle sizes of pure Ni powder and as-prepared Ni–Al alloy powder were measured using a particle size analyzer (Horiba LA300).

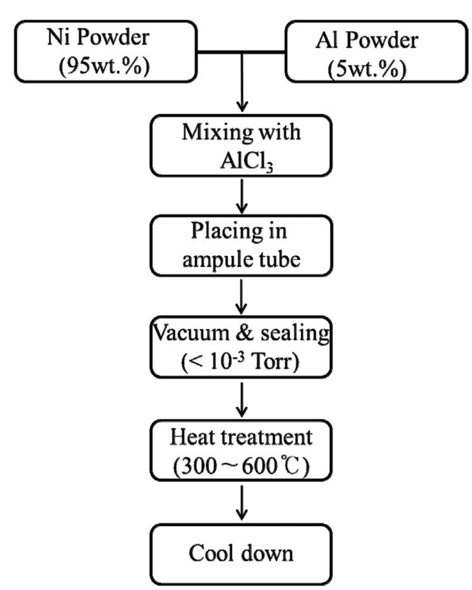

Fig. 1 – Procedure for the fabrication of Ni–Al alloy powder using $AlCl_3$ activator.