Mechanistic Insight into Electrochemical Synthesis of LaNi₅ in a Eutectic CaCl₂-NaCl Melt at 850 °C

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LaNi₅ alloy powders were prepared by electro-deoxidation of the oxide precursors in a eutectic CaCl₂-NaCl melt at 850 °C. The reduction pathway from the mixture of LaNi₅Oₓ and NiO to LaNi₅ was studied by examination of partially reduced samples using XRD, SEM and EDX analysis, which were obtained by interrupting the reduction process after different reduction times. The first stage of the reaction involved the rapid formation of Ni and of LaOCl, then LaOCl and La₃O₇ were electrochemically reduced and alloyed with Ni particles nearby along with their surface. The morphology of LaNi₅ particles reduced for the different durations of reduction can be changeable.

Key Words : LaNi₅, Alloy, Molten Salt, Electrochemical Synthesis, LaOCl

1 Introduction

LaNi₅ alloy is a typical kind of hydrogen-storing material. It has been widely adopted for the electrode materials of Ni-MH batteries because of its high capacity of absorbing hydrogen rapidly and reversibly near atmospheric pressure at room temperature. At present, the LaNi₅ alloy can be produced on industrial scale by separately extracting and refining the individual metals, followed by melting, alloying and casting under vacuum. The complex processes with high energy consumption and low production efficiency make the overall cost of conventional production of LaNi₅ very high. Therefore, an easier, less expensive and more environmentally friendly process for production of LaNi₅ hydrogen storage alloy is highly desired. There have been a lot of researches about synthetic routes and property characterization of LaNi₅ alloy.

In the past few years, a novel electrochemical process has been developed, in which some metals and alloys are obtained through direct electrochemical reduction of the respective oxides in molten salts, which is called FFC process. Recently, the successful electrochemical reduction of La₃O₇ and NiO powders to LaNi₅ alloy in molten CaCl₂ was reported by Chen et al. There are some difficulties in producing LaNi₅ by FFC process, such as La₃O₇ with high hygroscopicity and the pulverization of the oxide precursor as a cathode. The latter problem is likely because of spontaneous reaction: La₃O₇ + CaCl₂ → 2LaOCl + CaO as mentioned in the literature. Fortunately, Chen et al. just solved both the former problems by sintering the mixture of NiO and La₃O₇ at 1200°C or higher to form compounded oxides, which is moisture insensitive and stable in molten CaCl₂. However, the mechanism of the electrochemical reduction of the oxide precursors to LaNi₅ is still ambiguous at present. More understanding of the mechanism for this process will be helpful to overcome the obstacles of preparation of LaNi₅ on the commercial-scale by employing FFC process.

In this work, LaNi₅ was prepared by electro-deoxidation from the mixture of La₃Ni₅Oₓ and NiO at 850°C in a eutectic CaCl₂-NaCl melt, which is a good alternative for pure calcium chloride because of its relatively low melting point. The possible reaction pathway of the electro-deoxidation was gained by examination of the partially reduced samples after different reduction times through X-ray diffraction and scanning electron microscopy equipped with energy-dispersive X-ray analysis.

2 Experimental

The chemicals in this study were of analytical reagent grade. La₂O₃ and NiO (La : Ni = 1.1 : 5) powders were ball-milled with anhydrous ethanol for 4 hours. Around 1.5 g of the mixture was pressed into a cylindrical pellet under 10 MPa (~15 mm diameter and 1.5-2.0 mm thickness), and then the oxide pellets were sintered in air at 1200°C for 4 hours. The electrolyte was the mixture of anhydrous calcium chloride and sodium chloride (CaCl₂ : NaCl = 1 : 1), prepared by slow heating to 350°C, and holding at this temperature for more than 48 hours, then melted in an alumina crucible. The pre-electrolysis of the molten salt electrolyte was performed at 850°C for 1 hour at the voltage of 2.5 V using two graphite rods as an anode and a cathode, respectively. After the pre-electrolysis, the sintered oxide pellet was immersed in the melt as a cathode instead of the graphite cathode in the pre-electrolysis. The electrode leads were Kanthal wires. Each electrochemical reduction experiment consisted of two stages. Initially, the potential of 3.1 V was applied between the oxide cathode and graphite rod anode for 1 hour. Thereafter, the applied potential was raised to 3.5 V and kept constant for different times. The reduction time mentioned in this paper is the total duration for the two stages. After termination of the reduction, the par-
tially or whole reduced sample was lifted from the melt and cooled to room temperature. Thereafter, the sample prepared was rinsed with water thoroughly and dried in ambient air at room temperature. The experimental apparatus used here was similar to that described in the literature.\textsuperscript{10} Morphology of the sintered and reduced pellets was investigated by means of an SSX-550 scanning electron microscope (SEM) equipped with energy-dispersive X-ray analysis. Phase analysis of samples was carried out with a D/Max-2500PC X-ray diffractometer (XRD) with Cu Kα radiation.

3 Results and Discussion

Figure 1 shows the XRD pattern and SEM image of the La\textsubscript{3}O\textsubscript{2}-NiO pellet sintered at 1200°C for 4 hours in air. NiO and La\textsubscript{3}Ni\textsubscript{2}O\textsubscript{5} are present in the sintered pellet according to its typical XRD pattern, and the particle size is about 1 μm. It indicates the compounded oxide can be formed by sintering the mixture of La\textsubscript{3}O\textsubscript{2}-NiO at 1200°C, which is in agreement with the results of the literature.\textsuperscript{12}

In order to examine the stability of compounded oxide, La\textsubscript{3}Ni\textsubscript{2}O\textsubscript{5} in the melt at the working temperature, the sintered La\textsubscript{3}O\textsubscript{2}-NiO pellet containing La\textsubscript{3}Ni\textsubscript{2}O\textsubscript{5} was simply submerged in the CaCl\textsubscript{2}-NaCl melt at 850°C for 8 hours. Figure 2(a) is the XRD pattern of the sample without any washing after being submerged. It shows there exist LaOCl and Ni, in addition to CaCl\textsubscript{2} and NaCl, and that no La\textsubscript{3}Ni\textsubscript{2}O\textsubscript{5} detected. That means La\textsubscript{3}Ni\textsubscript{2}O\textsubscript{5} is likely to react with Cl\textsuperscript{-} in the melt, and decompose to the simple oxides, which should be expressed as in equation (1).

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2\text{La}_3\text{Ni}_2\text{O}_5(s) + 6\text{Cl}^- = 6\text{LaOCl}(s) + 2\text{NiO}(s) + \text{Ni}_2\text{O}_3(s) + 30^2^- \quad (1)
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But, it is very puzzled that NiO or Ni\textsubscript{2}O\textsubscript{3} in the sample is hardly observed from its XRD pattern, while a lot of nickel exists. This is probably because of creation of a galvanic cell between the Fe-containing current collector and the Ni-oxide precursors in the pellet, as explained by Ben Jackson at al\textsuperscript{11} for the similar phenomenon about their research on production of TiNi by FFC process. When the Ni-oxides and Fe are placed in contact with each other, Fe will be preferentially oxidized to FeO, and NiO will be selectively reduced to Ni.

The sintered La\textsubscript{3}O\textsubscript{2}-NiO pellet was also submerged for 8 hours in the molten CaCl\textsubscript{2}-NaCl, which was pre-electrolyzed with application of 2.5 V for 1 hour at 850°C. Figure 2(b) shows the XRD pattern of the sample. The same phases present in the melt without pre-electrolysis are also present in the pre-electrolyzed melt. There is elemental nickel observed as the Ni-containing phase. There may be another reason for the formation of Ni in the pellet within the pre-electrolyzed melt. Usually, there should be some calcium existing in the CaCl\textsubscript{2}-NaCl melt after the melt pre-electrolysis, since CaO, as an inevitable impurity in CaCl\textsubscript{2}, can be decomposed when the voltage of 1.6 V or higher is applied between the two graphite rods in the molten CaCl\textsubscript{2}-NaCl during the pre-electrolysis. Therefore, nickel can be gained by reduction of the Ni-oxides. LaCl\textsubscript{2} is more stable than La\textsubscript{2}O\textsubscript{3} and La\textsubscript{3}Ni\textsubscript{2}O\textsubscript{5} in the molten CaCl\textsubscript{2}-NaCl, and withstands aggression of the melt. Fig. 3 illustrates the morphology of the sample which was washed thoroughly by water after being immersed in the molten CaCl\textsubscript{2}-NaCl. The morphology of

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\text{Fig. 2} \quad \text{XRD patterns of the samples immersed in the molten CaCl}_2\text{-NaCl (a) without pre-electrolysis and (b) with pre-electrolysis at the constant voltage of 2.5 V for 1 h at 850°C.}
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\text{Fig. 3} \quad \text{The SEM image of the sample as same as Fig. 2(a).}
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the particles is changed obviously compared with that of the as-sintered oxide precursors, which marks the appearance of quadrate flakes instead of some round nodules in the as-sintered pellet. According to the EDX analysis, the quadrate flakes contain LaOCl mainly and the round-shaped particles are of the overwhelming Ni.

Figure 4 shows a summary of the XRD analysis results for the partially and whole reduced products. For 1.5-hour and 2-hour reduction samples, their XRD patterns show LaOCl, La(OH)₃, and Ni. La(OH)₃ remained in the samples should be a derivative of La₂O₃ washed in water, and LaOCl is the product of reaction between the lanthana and chlorides in the melt. At the same time, almost all Ni-oxides are preferentially reduced to Ni within the pellet, which are similar to the published work on production of TiNi from NiTiO₃. When the electrochemical reduction was performed for 4 hours, LaNi₅ was becoming an overwhelming phase in the pellets, which can be observed in Fig. 4(c). It can be deducted that LaOCl and La₂O₃ can be cathodically reduced to La and alloyed with Ni in situ. After a 6-hour reduction, the pellet was fully reduced, which XRD pattern is shown in Fig. 4(d), and no other phase is observed except LaNi₅.

The morphological change of the particles in pellets during the reduction was investigated by analysis of their SEM images. Fig. 5(a) is the SEM image of 1.5-hour reduction pellet. The morphology of the particles near the surface of the pellet is as shown in Fig. 3, in which the flakes are LaOCl and round-shaped particles are nickel according to the EDX analysis. But there are a lot of particles with the flower shape near the core of the same pellet, which contains La, O and minor amount of Cl by the EDX analysis. They should be La(OH)₃ derivate from La₂O₃, probably because percolation of the CaCl₂ and NaCl is less effective within the pellet, and there are not much more amount of Cl⁻ to react with La₂O₃ and form LaOCl in the core of the 1.5-hour reduction sample. Fig. 5(b) shows the morphology of the 2-hour reduction sample. Although the same phases present in 1.5-hour reduction sample are also present in 2-hour reduction sample shown in Fig. 4, the reduction evolution can be found in the SEM image of the 2-hour reduction sample shown in Fig. 5(b). The vivid phenomenon of alloying can be observed especially in the upper-left inset in Fig. 5(b), which is the enlarged image of the boxed region in the same future. The particle with the shape of a center-empty pane should be a residue of LaOCl after being reduced and alloyed for 2 hours because it contains major La, O, Cl, and minor Ni by EDX analysis and the LaOCl particles have a variety of quadrate shapes before the reduction as shown in Fig. 3 and Fig. 5(a). One edge and corner of the pane connects with two other particles which both contain nickel predominantly. The connection at the corner is just a ligament for bonding the LaOCl particle to the nickel one.

Figure 5(c) showed the morphology of the 4-hour reduction sample. The particles are round-shaped, and some can reach up 5 μm in size. Further more, the particles have rough surfaces and seem 'cauliflower'. By combining the results of its XRD pattern shown in Fig. 4(c), these particles should be composed of LaNi₅. As the preferential reduction of the Ni-oxides mentioned previously, the as-reduced La from LaOCl or La₂O₃ would alloy with Ni particles nearby along with its surface. Surface alloying for the 4-hour reduction sample should be the key reason why the alloy particles have rough surfaces.

The morphology of the 6-hour reduction sample is shown in Fig. 5(d) which is much similar as shown in Fig. 5(c). But the surface roughness of the particles is becoming smoother, and the drive-force should be surface energy minimization. As explained in literature, the fast long-range atomic mobility in LaNi₅ leads crystal-lite size to increase dramatically with temperature and the lattice strain to drop quickly when the annealing temperature is above 350°C. Since the electrochemical reduction was performed in the molten CaCl₂-NaCl at 850°C and the reduced LaNi₅ pellets were still immersed in the melt before termination of the experiment manually, the molten salt electrolyte could provide the micro-gravity field besides the annealing buffer, which are both the favorable conditions for crystallite generation and lattice strain relaxation within the pellets. Therefore, the
duration of reduction performed will affect the morphology of the LaNi₅ particles strongly within the pellets.

4 Conclusion
LaNi₅ alloy is prepared successfully by electro-deoxidation from the La₂O₃-NiO starting material in the CaCl₂-NaCl melt at 850°C. The Ni-oxides are preferentially reduced to Ni in the oxide cathode, and the La-oxide can react with Cl⁻ in the melt spontaneously to LaOCl, which can be electrochemically reduced and alloyed with Ni to LaNi₅ in situ. The micro-morphology of LaNi₅ products changes with the duration of reduction in the molten CaCl₂-NaCl.

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