

Synthesis of LaNi₅ Alloy by Electro-deoxidation

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Abstract—LaNi₅ alloy was synthesized in the molten CaCl₂ electrolyte by the electro-deoxidation method at 850°C. The X-ray diffraction peaks indicated that La₂O₃-NiO oxide mixture formed LaNiO₃ and La₂NiO₄ during sintering at 1200°C for 2 h. Short time electro-deoxidation caused formation of LaOCl, Ni and LaNi₅. Upon extending the electro-deoxidation time LaOCl and Ni disappeared totally and there remained only target phase of LaNi₅.

Keywords—LaNi₅, Electro-deoxidation, XRD.

I. INTRODUCTION

There are extensive amount of works on the development of the high performance hydrogen storage alloy electrodes, the motivation being the utilization of these electrodes in the nickel metal hydride rechargeable batteries [1]. These alloy electrodes are generally synthesized by common methods like melting and grinding [2], mechanical alloying [3], chemical reduction [4] and electroless coating [5]. All these methods cover the synthesis of the alloys from pure elements. Recently it was reported that some metals and alloys can be obtained directly from their oxides in molten salts by the electro-deoxidation method [6]. This novel electrochemical process, which is also known as Fray-Farthing-Chen (FFC) Cambridge process, is accepted as revolutionary process since it provides great economical advantage especially if the multi-component alloy synthesis can be achieved.

In this work LaNi₅ alloy was synthesized by the molten salt electro-deoxidation method. The alloy development stages were characterized.

II. MATERIALS AND METHODS

Commercially available La₂O₃ and NiO powders (with at least 99.5% purity) were obtained from Alfa Aesar. Required amounts of the oxide powders were mixed homogeneously in anhydrous ethanol includes 3% (by weight) polyethylene glycol (PEG) with a planetary ball mill (Fritsch, Pulverisette P-7). The powder was then dried overnight at room temperature. Dried powder was cold pressed into pellets of 10 mm in diameter, under a pressure of 1.5 ton cm⁻². The oxide pellets were then sintered at 1200°C for 2 h.

The electrochemical experiments were performed in a quartz cell which was located inside a homemade programmable electrical furnace. The upper end of the quartz

cell was closed tightly with a quartz cover which has holes for the electrode leads, thermocouple, gas inlet and outlet. The quartz cell was continuously purged with Ar gas (100 - 150 ml min⁻¹) during the electro-deoxidation process.

100 gr CaCl₂ was mixed with 1 gr CaO and placed into graphite crucible. Before electro-deoxidation process CaCl₂-CaO powder mixture was dried under Ar gas. Drying was carried out by slow heating (about 1°C min⁻¹) to 150°C and holding at 150°C for 10 h and then slow heating to 300°C and holding at 300°C for 10 h and then finally slow heating to the target temperature of 850°C for the electro-deoxidation experiments.

In order to fully remove the water and the possible redox-active impurities, pre-electrolysis were carried out at 1.5 V and 850°C for 4 h. During the pre-electrolysis graphite crucible was used as anode and another graphite rod was used as cathode. For the electro-deoxidation experiments the graphite rod was removed from the cell and the prepared oxide pellet electrode was inserted into the quartz cell as a cathode.

After the electro-deoxidation experiments the pellet electrodes were removed from the molten melt and they were located in the upper part of the quartz cell which was cooled down by keeping the Ar gas purging. The solidified salt on the pellet was washed out by tap water. After slight surface grinding the pellets were kept in 1 M HCl for about 1 h. Finally the deoxidized pellet samples were dried at 100°C for 24 h under vacuum.

The phase structure of the alloy powders was examined by the X-ray diffractometer (Bruker axs D8) using Cu K α radiation. The powder morphologies were observed by ZEISS SUPRATM 50 VP Scanning Electron Microscope (SEM).

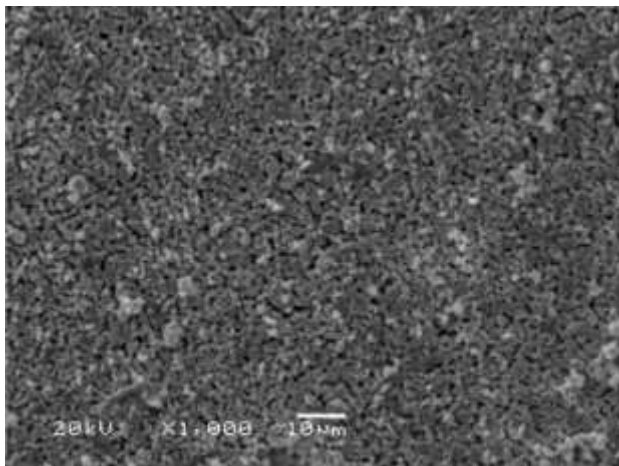
III. EXPERIMENTAL RESULTS AND DISCUSSIONS

Scanning electron micrographs of the as-sintered oxide powder and the deoxidized powder (for 10 h) are provided in Fig. 1. As-sintered powder has typical fine oxide powder appearance in Fig. 1a. At the end of 10 h electro-deoxidation process, however, the typical large crystalline metallic powder morphology develops as in Fig. 1b.

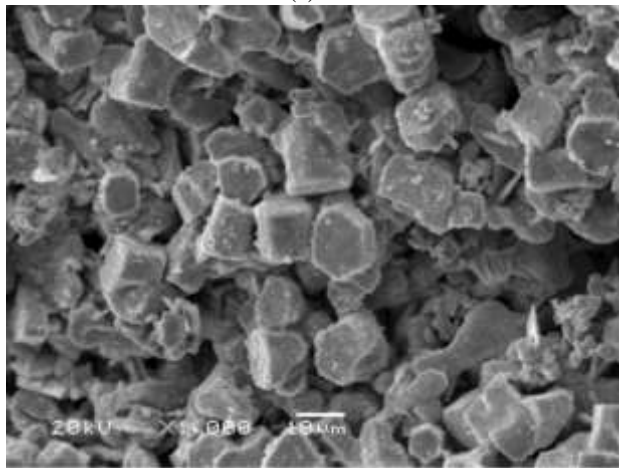
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(a)



(b)

Fig. 1 Powder morphologies after (a) sintering and (b) electro-deoxidation for 10 h.

The overlaid X-ray diffraction (XRD) patterns of the as-sintered, 2 h, 5 h and 10 h deoxidized powders are shown in Fig. 2. As-sintered powder has peaks of La_2NiO_4 , LaNiO_3 and NiO . Since La_2O_3 is hygroscopic the formation of non-hygroscopic La_2NiO_4 and LaNiO_3 oxides during sintering is very crucial for the electro-deoxidation process [7]:



The deoxidation up to 5 h, in Fig.2, causes formation of LaOCl , $\text{La}_4\text{Ni}_3\text{O}_9$ and metallic Ni in addition to the target phase LaNi_5 :

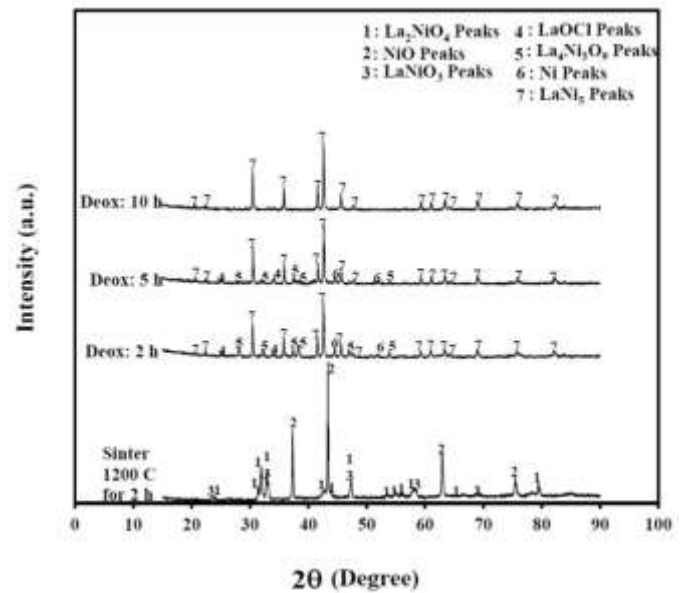
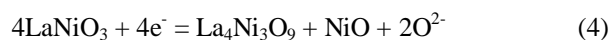
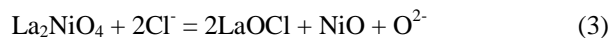
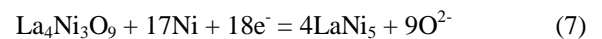


Fig. 2 XRD patterns of the samples after sintering and electro-deoxidation for 2 h, 5 h and 10 h.



Upon extending the electro-deoxidation time up to 10 h, there remains only target LaNi_5 phase. Since sintering has already brought together La and Ni atoms by forming La_2NiO_4 and LaNiO_3 oxides, the formation of La-Ni final phase is relatively faster. Obviously the electro-deoxidation provides economical pathway to synthesize commercial hydrogen storage alloys especially the large scale applications (like the battery systems of electrical vehicles) are considered.

IV. CONCLUSION

It was clearly showed by providing the LaNi_5 alloy development stages that electro-deoxidation method is effective and considerably economical way to synthesize the hydrogen storage alloys.

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