Effect of composition and particle morphology on the electrochemical properties of LaNi$_5$-based alloy electrodes

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ABSTRACT

Al and Co substituted LaNi$_5$-based intermetallic compounds were investigated as negative electrode materials in alkaline KOH-electrolyte. The structure, morphology and electrochemical properties of gas-atomised and cast LaNi$_{4.5}$Al$_{0.5}$ and LaNi$_{2.5}$Co$_{2.4}$Al$_{0.1}$ alloys were investigated and the effect of the substitutions and the production method on the surface and bulk composition is compared to cast LaNi$_5$ as a reference.

While the rapid solidification of the gas-atomised alloys affects the site energy distribution for hydrogen on the interstitial sites, the activation and degradation mechanism of the electrodes cycle life is dominated by the elemental composition of the alloy and especially the surface. Therefore, the alloys with the larger Al content activate within a few cycles and also degrade faster as compared to the alloys with a high Co content. Furthermore, the dissolution of Al leads to a highly active surface with a lower reaction resistance, which leads to an order of magnitude increased high rate dischargeability.

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1. Introduction

LaNi$_5$-based alloys are used widely as a material for the negative electrode in Ni-MH rechargeable batteries. The nickel metal hydride system has advantages as an electrode material for secondary batteries because of its high energy density, tolerance to overcharging, good high-rate capability and environmental safety [1–4]. However, the basic intermetallic LaNi$_5$ alloy cannot be used in these batteries because of its low cycle stability and the high self-discharge of the electrodes. Partial substitution of Ni by such elements as Co, Al or Mn can significantly improve the cycle stability and high discharge capacity of the electrodes [5–10]. In order to reduce the price of the alloy, La is commonly substituted by mischmetal (Mm) [2,3]. Currently, the composition of the commercial alloy for Ni-MH batteries contains all of these elements, i.e., it is Mm(NiCoAlMn)$_5$ [3,4,11].

The composition and the technology of the alloy fabrication influence the surface composition and therefore the kinetics, hydrogen storage properties and especially the stability of the alloy electrodes [12,13].

High-pressure gas atomisation (HPGA) is an economic fast and reproducible method for the production of well-defined AB$_5$ type alloy particles. Gas-atomised alloy particles exhibit enhanced corrosion resistance, i.e., they show excellent electrochemical cycle stability [13]. The technology produces a large amount of alloy powders from a wide range of possible particle sizes with a uniform alloy composition and well-defined surface composition. Furthermore, the cost of the standard route for manufacturing AB$_5$-type materials can be reduced by using this technology, which includes the following initial steps: (1) melting and chill casting of large ingots; (2) extensive heat treatment of the ingots to eliminate microscopic compositional inhomogeneities; and (3) grinding of the annealed ingots into fine powders, which might include hydriding and dehydriding to fracture large ingots into smaller pieces [14,15].

However, it is still not clear exactly how this technology changes the electrochemical and storage characteristics of alloy electrodes. One group of authors has indicated that gas-atomised alloys have hydrogen storage gas capacities and equilibrium pressures nearly identical to cast alloys [16]. Lim et al. reported that gas-atomised alloy electrodes show lower specific capacity and slower activation with cycling than corresponding non-atomised alloys [17]. It is also reported that short-term annealing and chem-
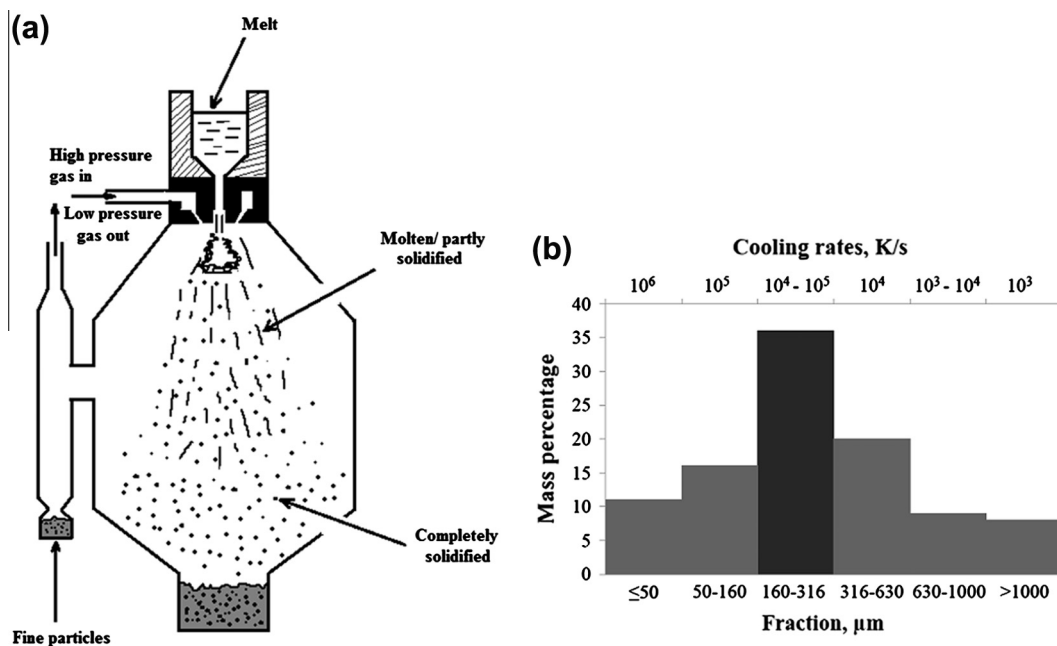
Fig. 1. Schematic illustration of the high-pressure gas-atomisation process (a) and particle size distribution [15] of gas-atomised alloy powders with indicated cooling rates (b).

ical surface activation can improve substantially the characteristics of gas-atomised powders [14,16–19].

Therefore, it is of interest to investigate the possibility of using gas-atomised powders in Ni–MH batteries. Previously, we have shown the dependence of activation, kinetics of reversible hydrogen sorption and discharge capacity of gas-atomised $LaNi_{4.5}Al_{0.5}$ alloy electrodes from the used alloy fraction. These characteristics depend on the state and composition of the surface of the alloy particles [20].

It has been reported that Al and Co affect the cycle life in different ways and that both elements synergistically improve electrode cycle life [5]. It appears that Co improves the cycling stability with regard to the mechanical properties and Al improves it with reduced lattice expansion and reduction of the equilibrium pressure of hydride formation.

In this paper, we investigate the electrochemical and storage characteristics of electrodes from two gas-atomised $LaNi_5$-based alloys with the composition: $LaNi_{4.5}Al_{0.5}$ and $LaNi_{2.5}Co_{2.4}Al_{0.1}$ of the same particle size fraction (160–316 μm) to explore the effect of Ni substitution by Al and Co. Furthermore, we compare the electrochemical and morphological properties of gas-atomised $LaNi_{4.5}Al_{0.5}$ and $LaNi_{2.5}Co_{2.4}Al_{0.1}$ alloys with cast alloys of the same composition and $LaNi_5$ as a reference compound.

2. Experimental

2.1. Alloy preparation

Two compositions ($LaNi_{4.5}Al_{0.5}$ and $LaNi_{2.5}Co_{2.4}Al_{0.1}$) of alloys were prepared by high-pressure gas atomisation of a melted alloy in argon. A schematic illustration of this process is shown in Fig. 1a. From the tundish at the top of the atomiser, a continuous melt stream passes through a gas nozzle where it impinges a high-pressure argon gas jet and thereby breaks into droplets. The process parameters are as follows. Temperature of the melt: 1450 °C, gas pressure: 1.25 MPa for $LaNi_{4.5}Al_{0.5}$ and 0.7 MPa for $LaNi_{2.5}Co_{2.4}Al_{0.1}$, gas temperature: 630 °C, melt flow: 0.6–0.7 kg/min, weight of one powder batch: 25 kg [15]. To obtain the same particle size distribution for investigated alloys experimentally was determined that for Co-containing alloy at the same gas temperature the gas pressure should be approximately twice lower. After preparation, all powders were sieved and sorted into fractions. The particle size distribution of these gas-atomised (GA) alloy powders is presented in Fig. 1b. We investigate the difference of electrochemical
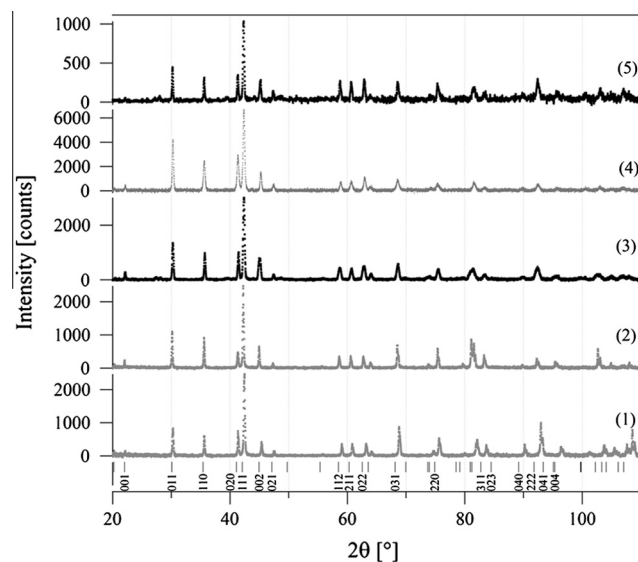

Fig. 2. XRD patterns: (1) $LaNi_5$ cast, (2) $LaNi_{4.5}Al_{0.5}$ cast, (3) $LaNi_{4.5}Al_{0.5}$ gas-atomised, (4) $LaNi_{2.5}Co_{2.4}Al_{0.1}$ cast, and (5) $LaNi_{2.5}Co_{2.4}Al_{0.1}$ gas-atomised alloy powders.

behavior of two alloys of the most distributed alloy fraction: 160–316 μm. The cooling rate of the powders of this fraction is about 10^4–10^5 K/s (Fig. 1b), which is close to the hardening conditions of the material [15]. According to the chemical analysis data, the investigated fraction powders contain about 0.1 wt.% oxygen.

2.2. XRD of alloys and hydrides

X-ray diffraction (XRD) measurements of all samples were performed using a Bruker D8 Advanced diffractometer (Cu Kα radiation, λ = 1.54184 Å, tube parameters: V = 40 kV, I = 40 mA) with a parallel incident beam prepared by a Göbel X-ray mirror. The patterns were recorded with a 1D position sensitive detector (VÅNTEC). The powder samples were measured using a flat sample holder in reflection mode. The scans were recorded in the 2θ range 20–120° at room temperature. Typical scan speeds were 0.5°/min. Quantitative phase analysis was performed using TOPAS 4.2 from Bruker AXS.