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Gas atomized powders of hydride-forming alloys and their application in rechargeable batteries

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Abstract

Gas atomized powders of $LaNi_{4.5}Al_{0.5}$ and $LaNi_{2.5}Co_{2.4}Al_{0.1}$ alloys were prepared and separated into fractions with different particle sizes. The dependence of morphology, oxygen content and crystal structure of the powders on particle size have been analyzed by means of XRD, SEM and EDS. The hydriding and electrochemical properties of different fractions were also evaluated. All fractions had a similar particle morphology and X-ray lattice parameters. EDS of the gas atomized alloys indicated that the surface of the smaller particles was less contaminated by oxygen than course particles. At the same time the fractions with particle sizes below 50 μm had poor activity both for gas hydrogenation and electrochemical charging. On the DTA curve of the small particles fraction an additional exothermal peak was observed, which may be attributed to a thermal-induced crystallization of the more developed amorphous component of the small particles structure. Gas atomized powders having large particle sizes display hydrogen and electrochemical capacity similar to those of arc-melted alloys.

Keywords: Hydrogen; Intermetallics; Alloys

1. Introduction

During gas atomization of liquid metals very high cooling rates of up to 10^6 K s^{-1} can be achieved and peculiar structures of powders having fine grains and an amorphous component can be obtained [1,2]. Powders of the hydride-forming alloys with such structures possess enhanced corrosion resistance [3] and seem to be promising materials for negative electrodes of nickel/metal hydride batteries [4,5]. Hydride-forming intermetallic alloys involve La(Mm) or Zr and are very reactive. In molten state these alloys react with oxygen, nitrogen, moisture and crucible materials. Besides, powders of these alloys are also reactive at ambient temperature if exposed to oxygen or air. At the same time powder metallurgical routes for large-scale production of hydride-forming materials for nickel/metal hydride batteries could be highly productive and economically attractive. The structure peculiarities and electrochemical properties of the gas atomized powders of hydride-forming alloys have not yet been studied thoroughly. In this investigation, gas atomized powders of $LaNi_{4.5}Al_{0.5}$ and $LaNi_{2.5}Co_{2.4}Al_{0.1}$ alloys have been prepared and particle size distribution, morphology, crystal structure, oxygen location, hydriding and electrochemical properties have been evaluated.

2. Experimental details

The powders of the $LaNi_{4.5}Al_{0.5}$ and $LaNi_{2.5}Co_{2.4}Al_{0.1}$ alloys were prepared using the Ar gas atomization method. The parameters of the process 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^{-1}; the weight of one powder batch, 25 kg. The initial product was separated into fractions with different mean particle size. For the separation and the determination of the particle size distribution the conventional sieve method was used. The dependence of the structural, hydriding and electrochemical characteristics on particle size have been investigated. For the structural investigations X-ray analysis, SEM and energy dispersive spectroscopy (EDS) were used. The structure changes taking place during heating of the powders were estimated using the Differential Thermal Analysis (DTA) and Thermal Gravimetric Analysis (TGA) methods. The gas hydriding of the alloys was studied in

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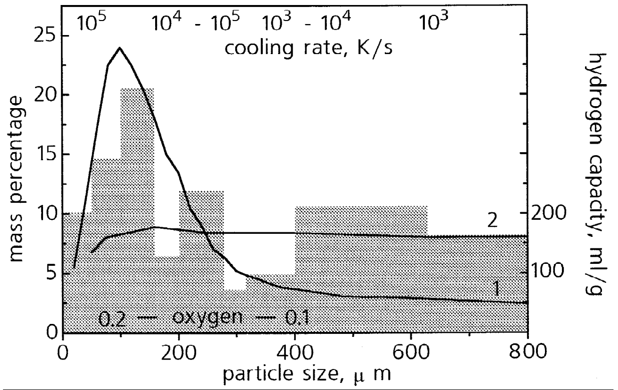

Fig. 1. (1) Particle size distribution for gas atomized $LaNi_{4.5}Al_{0.5}$ powders, and (2) dependence of hydrogen capacity on particle size.

the conventional Sievert's apparatus. The electrochemical charge–discharge experiments were performed using an automated 70 channel apparatus with computer-assisted processing and analysis of the data. The small 11.6×4.2 mm sealed cells, 6 M KOH electrolyte solution and $Ni(OH)_2$ counter electrode were used. The weight of the electrode was 0.1 g. The charge current was 3 mA and the time of charge was 12 h. The discharge was carried out at 3 mA up to 1.0 V potential with reference to $Ni(OH)_2$.

3. Results and discussion

The gas atomized powders of both alloys investigated exhibit a similar particle size distribution with a maximum located at 100 μm. The mass distribution determined for $LaNi_{4.5}Al_{0.5}$ is presented in Fig. 1. The chemical analysis indicates that the coarse fractions contain approximately 0.1 wt% O_2. The fine fractions with particle size less than 50 μm contain about 0.2 wt% O_2. The smaller fractions also demonstrate lowered hydrogen capacity (Fig. 1, curve 2) and require more vigorous activation conditions during gas hydriding. For example, the coarse fractions show the nominal maximum hydrogen capacity during the first cycle without any activation. At the same time fraction '−50 μm' had to be activated at 200 °C and produced the nominal hydrogen capacity only after several cycles.

The X-ray structure analysis indicates that all fractions of both alloys have the same $CaCu_5$-type structure. The dependence of the lattice parameters on particle size is shown in Table 1.

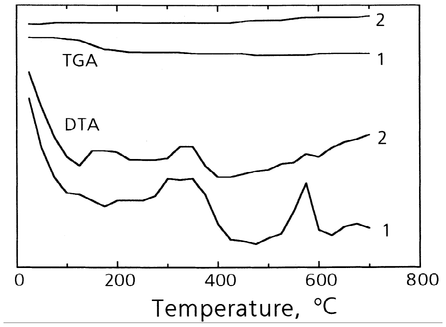

Fig. 2. DTA and TGA of the gas atomized $LaNi_{4.5}Al_{0.5}$ powders: 1, '−50 μm'; 2, '+316–400 μm'.

The X-ray data show only a small increase of the lattice parameters when going from the fine to the coarse fractions. A difference between fine and coarse fractions was also observed using the DTA and TGA methods (Fig. 2). On the DTA curve an additional strong exothermal peak at 560 °C (heating rate, 10 $K\,min^{-1}$) was observed for the fraction '−50 μm'. The TGA result showed no weight loss in this temperature range. The DTA measurements were performed at two heating rates 5 $K\,min^{-1}$ and 10 $K\,min^{-1}$. The activation energy E was determined by means of measurement of exothermal peak shift depending on the heating rate [6,7] and found to be $E=230\pm20$ $kJ\,mol^{-1}$. Similar values were obtained for the crystallization of some amorphous alloys [7].

In Fig. 3. the results from EDS analysis of the surface of small and coarse particles of $LaNi_{4.5}Al_{0.5}$ are presented. As mentioned before, the fine fractions contain more oxygen, nevertheless the EDS peak intensity in Fig. 3a for a small particle is smaller then the oxygen peak in Fig. 3b from a coarse particle. This fact can be explained by considering the rates of cooling and oxidation as functions of particle size, and assuming a parabolic dependence of the oxide layer thickness h on time t: $h^2=K\times t$. The cooling time of the particle to a temperature (t), where oxidation is impossible depends on the particle volume and surface as shown by the relation: $t=K_1\times V/S$, leading to $h\sim r^{1/2}$, where r is the particle radius.

According to this model the mean oxygen concentration in certain powder fractions may be presented as $c\sim r^{-1/2}$.

Table 1

Alloy	Lattice parameter: a, c (nm), V (10^3 nm)	−50 μm	+50–630 μm	+630 μm
$LaNi_{4.5}Al_{0.5}$	a	0.5037	0.5040	0.5041
	c	0.4034	0.4035	0.4038
	V	88.6	88.8	88.9
$LaNi_{2.5}Co_{2.4}Al_{0.1}$	a	0.5088	0.5091	0.5091
	c	0.4032	0.4033	0.4035
	V	90.4	90.5	90.6

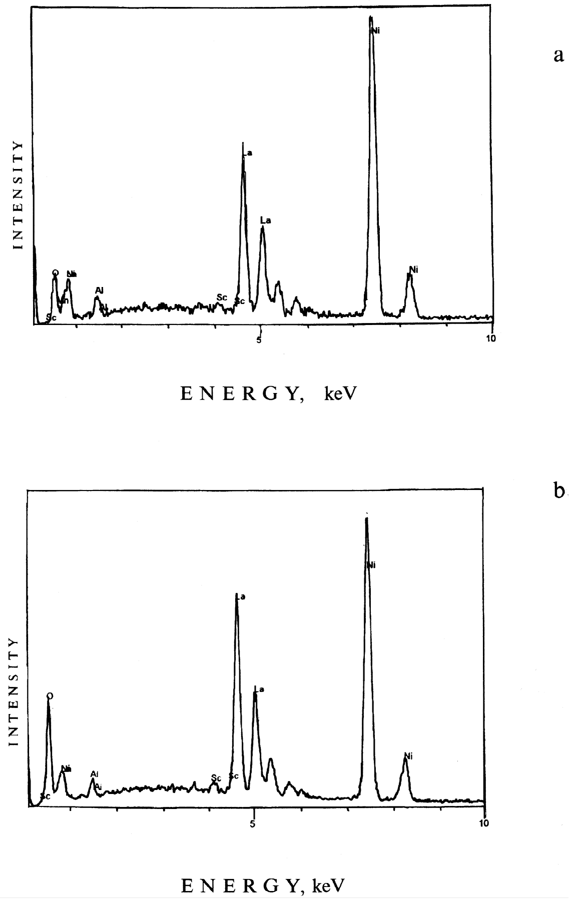

Fig. 3. EDS spectrum from the surface of $LaNi_{4.5}Al_{0.5}$ particles: (a) size 30 μm, and (b) size 200 μm.

Small particles undergo less oxidation owing to the higher cooling rate during gas atomization of the liquid alloy. Consequently the higher mean oxygen concentration in fine fractions can not explain the changes in their characteristics.

Fig. 4 shows the SEM images of the investigated powders. The surface of the particles have glass-like structure. The partial amorphization of the gas atomized powders may influence considerably the hydriding kinetics. The exothermal DTA peak of the small particles fraction may be attributed to a thermal-induced transformation of the more developed amorphous constituent of small particles into a crystalline form. The presence of an amorphous component in the powder causes a slowing in the hydriding kinetics. The hydrogen absorption in crystalline alloys involves a phase transition between a dilute solid solution and a concentrated hydride with an expanded lattice. The resulting interphase stresses induce an intensive cracking, an increase in surface area and additional reaction activation. Metallic glasses do not undergo any phase transition on absorbing hydrogen; the cracking and additional activation are not so intense [3].

The results from the electrochemical investigations of the gas atomized alloys are presented in Fig. 5a Fig. 5b.

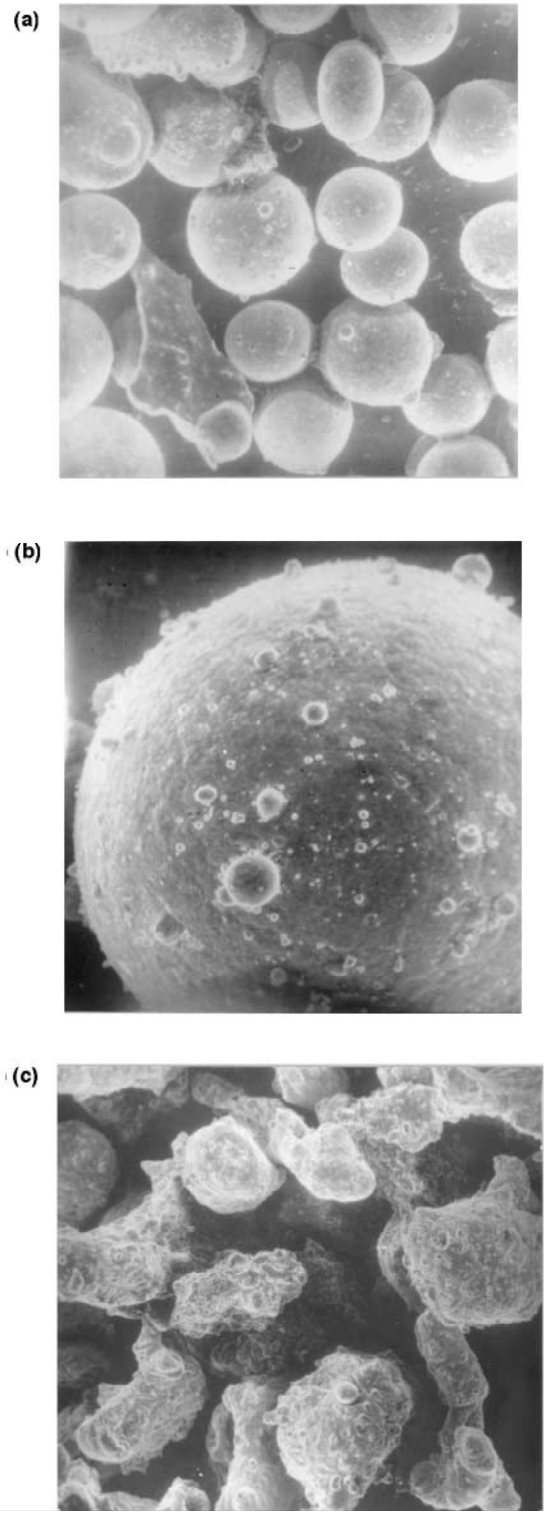

Fig. 4. (a) and (b) SEM images of the atomized $LaNi_{4.5}Al_{0.5}$, and (c) $LaNi_{2.5}Co_{2.4}Al_{0.1}$ powders.

The electrodes were prepared from the coarse fraction ‘160–316 μm’ and fine fraction ‘−50 μm’. The first one demonstrates the electrochemical discharge capacity on the level of arc-melted alloys.

On the base of gas atomized powders of

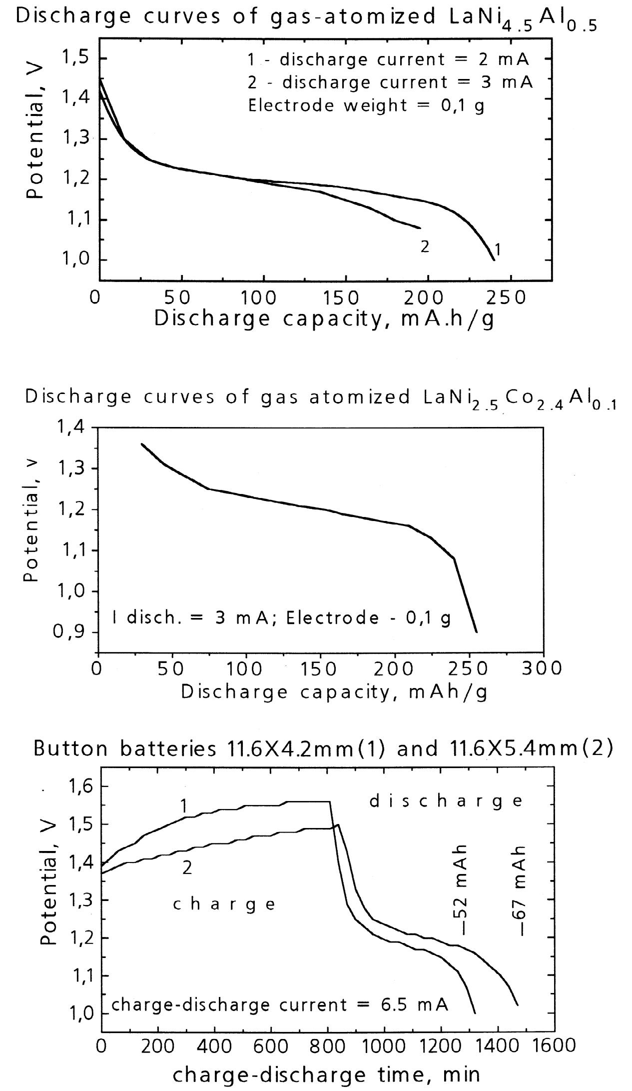

Fig. 5. Discharge curves (third cycle) for the (a) $LaNi_{4.5}Al_{0.5}$ and (b) $LaNi_{2.5}Co_{2.4}Al_{0.1}$ alloys (c) charge–discharge curves for batteries: 1, 11.6×4.2 mm; 2, 11.6×5.4 mm.

$LaNi_{2.5}Co_{2.4}Al_{0.1}$ (fraction '160–316 μm') electrodes and button nickel/metal hydride batteries of two types (11.6×4.2 mm and 11.6×5.4 mm) were constructed. Their charge–discharge curves are shown in Fig. 5c.

4. Conclusion

The structure, hydrogen absorbing and electrochemical properties of the gas atomized powders of $LaNi_{4.5}Al_{0.5}$ and $LaNi_{2.5}Co_{2.4}Al_{0.1}$ alloys depend on particle size. The finest powders need very strong activation conditions and have poorer gas hydriding and electrochemical characteristics. Powders of large particles sizes demonstrate a similar hydrogen absorbing ability as powders prepared from arc-melt alloys. The EDS analysis indicates that oxygen concentrates mainly on the particle surface. The surface of the small particles contains relatively less oxygen because of the high cooling rate during solidification. Gas atomized powders of coarse fractions possess good electrochemical performances.

Acknowledgments

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