



Partial substitution of cobalt for nickel in mixed rare earth metal based superlattice hydrogen absorbing alloy – Part 1 structural, hydrogen storage and electrochemical properties



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ABSTRACT

The structural, gaseous phase hydrogen storage and electrochemical properties of a series of cobalt-substituted superlattice alloys were investigated as Part 1 of a two-part series. The phase abundances, lattice parameters and unit cell volumes of the AB₅, AB₃ and A₂B₇ phases were analyzed by X-ray diffraction patterns. Cobalt (Co) has a more noticeable effect on promoting the AB₅ phase than manganese (Mn) and increases both the gaseous phase hydrogen storage and electrochemical capacity of the alloys. It does this by forming more stable hydrides with a lower pressure-concentration-temperature plateau pressure and a more negative heat of formation. The decreasing entropy difference also indicates that Co promotes a more ordered hydride. An alloy with 7 at% Co shows the best high-rate electrochemical performance due to the increased hydrogen diffusion coefficient and exchange current density. Magnetic susceptibility measurements indicate that there are other factors besides the surface nickel (Ni) cluster that dominate the high-rate performance of the Co-substituted superlattice alloys.

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1. Introduction

Superlattice hydrogen absorbing alloys (HAA) have been extensively studied in academia (for a recent review, see Ref. [1]) and they have also been used in both the consumer and hybrid electric vehicle market [2,3] because of their superiorities in capacity [4], high-rate performance, self-discharge [5] and cycle stability [6] compared to the currently used AB₅ HAA [7]. Compared to AB₂ (another high capacity HAA family), superlattice alloys show improved high-rate performance due to their higher concentration of catalytic metallic Ni on the surface [8].

By stacking one, two, three or four slabs of AB₅ units between A₂B₄ slabs, superlattice alloys with B/A ratios from 3 to 4 can be obtained (Fig. 4 in Ref. [1]). While A sites in the superlattice AB_x HAAs are occupied by rare earth (La, Ce, Pr, Nd, Sm, etc.) and alkaline earth elements (Mg and Ca) with relatively larger atomic

radii, B sites are mainly occupied by transition metals with smaller size atomic radii. In the A-site atoms, La contributes to the superior capacity of the alloys by averaging down the hydrogenation enthalpy; other rare earth metals are used to improve the cycle life and charge retention [1] while alkaline earth metals are used for the reduction of the average metal–hydrogen bond strength and destabilization of the hydride. While many modifying elements have been tried in the B-site of superlattice HAA, Al was found to be the only necessary partial substitution to Ni for the optimization of battery performance, especially in charge retention and cycle life [2]. The effects of Mn-substitution for Ni in the MmMgNiAl based Co/Mn-free superlattice alloys have been systematically studied and reported in a two-part series paper [9,10]. The incorporation of Mn results in lower hydrogen storage capacities in both the gaseous phase and electrochemistry. It also reduces the high-rate dischargeability (HRD) because of a decreased amount of catalytic metallic Ni inclusions on the activated alloy surface. However, the low-temperature performance and cyclic stability of the Mn/Co alloy are improved. As a necessary component of AB₅ alloys, Co increases the *c/a* ratio and therefore decreases the hysteresis and results in extended cycle life [11]. However, a systematic study of

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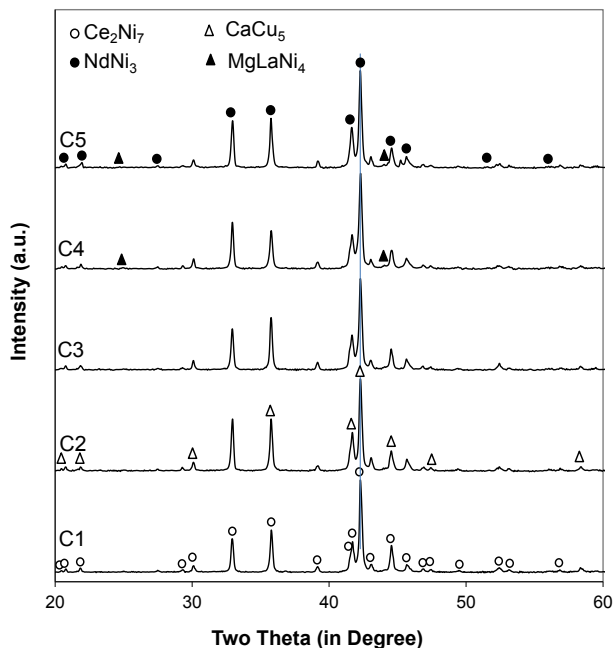


Fig. 1. XRD patterns using Cu-K α as the radiation source for alloys C1–C5.

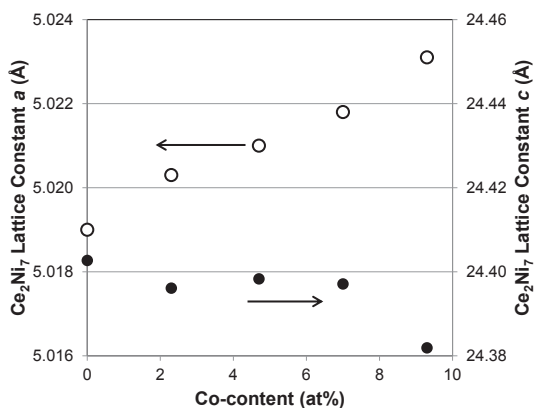


Fig. 2. Plots of Ce₂Ni₇-type phase lattice parameters *a* and *c* as functions of Co-content.

Co-substitution in Mn/Co-free superlattice alloys has not been reported. Therefore, it is significant to study the effects of Co on the mixed rare earth (MRE) metal based superlattice alloys. The phase abundance, crystal structure, metallic nickel distribution in the surface oxide layer and electrochemical properties of these Co-substituted superlattice alloys are discussed in Part 1 of this two-part paper. The evaluation of sealed-cell performance with the results of failure analysis of these Co-substituted superlattice alloys will be presented in Part 2.

2. Experimental setup

The designed alloys were produced by Japan Metals & Chemicals Co., Ltd. using an induction melting method. The chemical composition of the MRE metal is 19.6 wt% lanthanum (La), 40.2 wt% praseodymium (Pr) and 40.2 wt% neodymium (Nd). The alloy ingots were mechanically ground to –200-mesh powder and then pressed onto an expanded Ni substrate with no other additives. A Varian Liberty 100 inductively-coupled plasma (ICP) system was

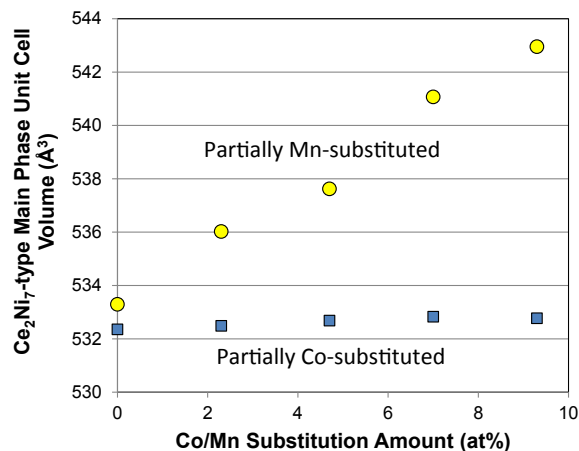


Fig. 3. Plots of Ce₂Ni₇-type phase unit cell volume of Co- and Mn-substituted alloys.

used to analyze the chemical compositions of the alloys. A Philips X'Pert Pro X-ray diffractometer (XRD) was used to examine the microstructures of the alloys. A JEOL-JSM6320F scanning electron microscope (SEM) with energy dispersive spectroscopy (EDS) capability was used to study the phase distribution and composition of each constituent phase. Pressure-concentration-temperature (PCT) isotherms were measured using a Suzuki-Shokan multi-channel PCT system. A Digital Measurement Systems Model 880 vibrating sample magnetometer was used to measure magnetic susceptibility.

Electrochemical properties were tested in flooded half-cells using an Arbin Battery Test System. The discharge capacity of each alloy was measured in a flooded-cell configuration against a sintered nickel hydroxide (Ni(OH)₂) positive electrode. The sintered Ni(OH)₂ electrodes were fabricated in-house and used as standard positive electrodes for our Ni/MH battery research. The electrolyte is 6 M potassium hydroxide (KOH) in deionized water. For the negative electrode, the alloy powders, typically weigh 60–80 mg with an accuracy of ± 0.1 mg, were pressed on a Ni mesh current collector with no binder or other additives, for better reproduction of the environment in a sealed cell. No alkaline pre-treatment was applied before the half-cell measurement, which is needed for AB₂ alloys. A constant current density of 100 mA g⁻¹ for 5 h was used to charge the as-prepared electrodes and then a current density of 100 mA g⁻¹ followed by two pulls at 25 and 8 mA g⁻¹ was used to discharge until a cutoff voltage of 0.9 V. In order to study the electrochemical kinetic properties of the alloys, in particular the diffusion coefficient of the hydrogen atoms in the bulk of the alloy and exchange current density at the surface layer of the alloy, potentiostatic discharge and linear polarization experiments were performed respectively. For potentiostatic discharge test, fully charged metal hydride electrodes were discharged at an overpotential of +0.6 V for 7200 s with the anodic current response recorded versus time. For linear polarization tests, metal hydride electrodes were fully charged and then discharged to 50% depth-of-discharge (DOD), followed by linear potential sweep in a small overpotential range of ± 10 mV vs. equilibrium potential at a scan rate of 0.1 mV/s. All these measurements were performed on an Arbin BT4 workstation.

3. Results and discussion

Five alloys (Mm_{0.83}Mg_{0.17}Ni_{3.14-x}Al_{0.17}Co_x, *x* = 0, 0.1, 0.2, 0.3, and 0.4) were designed with a fixed formula of AB_{3.31}, where Mm and

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