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Ti(Ni,Cu) pseudobinary compounds as efficient negative electrodes for Ni–MH batteries

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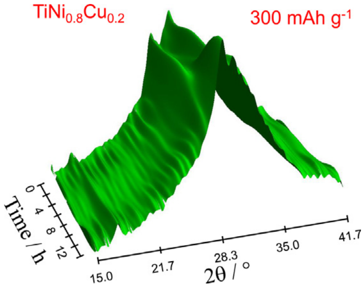
HIGHLIGHTS

- Hydrogenation properties of pseudobinary Ti(Ni,Cu) compounds are deeply investigated.
- Cu-substitution destabilizes the hydride phase and opens a wide miscibility gap.
- $TiNi_{0.8}Cu_{0.2}$ exhibits a high discharge capacity of 300 mAh $g^{-1}$with good cycle life.
- Electrochemical discharge capacities are two-fold higher than for binary TiNi.
- Ti(Ni,Cu) compounds are promising rare-earth free anodes for Ni–MH batteries.

GRAPHICAL ABSTRACT



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ABSTRACT

The effect of Ni by Cu substitution on the structural, solid–gas and electrochemical hydrogenation properties of TiNi has been investigated. Pseudo-binary $TiNi_{1-x}Cu_x$ ($x \leq 0.5$) compounds have been synthesized by induction melting. They crystallize in B2 structure above 350 K and either in $B19'$ ($x < 0.1$) or $B19$ ($0.2 \leq x \leq 0.5$) at room temperature (RT). For all compounds, Pressure-Composition Isotherms at 423 K exhibit a single slopping plateau pressure within the range 10^{-3}–1 MPa of hydrogen pressure revealing a metal to hydride transformation. Both the hydrogenation capacity and the hydride stability decrease with Cu-content. The hydrided pseudobinary compounds crystallize in the tetragonal S.G. *I4/mmm* structure as for TiNi hydride. The electrochemical discharge capacity increases with Cu content from 150 mAh g^{-1} for TiNi up to 300 mAh g^{-1} for $TiNi_{0.8}Cu_{0.2}$ and then decreases again for larger Cu amounts. Electrochemical isotherms and *in-situ* neutron diffraction measurements at RT demonstrate that such a capacity increase results from a metal to hydride phase transformation in which the hydride phase is destabilized by Cu substitution. The $TiNi_{0.8}Cu_{0.2}$ compound exhibits interesting cycling stability for 30 cycles and good high-rate capability at D/2 rate. This compound has promising electrochemical properties as compared to commercial $LaNi_5$-type alloys with the advantage of being rare-earth metal free.

1. Introduction

In the later decades, metal hydrides have deserved extensive research since they can store higher amount of hydrogen per unit volume under moderate conditions of pressure and temperature

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than high pressure tanks and liquid hydrogen [1,2]. Beside hydrogen storage applications, their use as active materials for the negative electrode of Ni–MH batteries is pursued [3–5]. Ni–MH batteries are a good alternative to Ni–Cd ones since the use of toxic cadmium is avoided and higher energy density (30–50%) is reached. Several metal-hydride forming compounds can be used in Ni–MH batteries such as $LaNi_5$ (AB_5), $La_{5-x}Mg_xNi_{19}$ (A_5B_{19}), $La_{2-x}Mg_xNi_7$ (A_2B_7), $La_{1-x}Mg_xNi_3$ (AB_3), $ZrNi_2$ (AB_2) and TiNi (AB), where A and B stand for metals forming stable and unstable hydrides, respectively [6]. Compounds of compositions ranging from AB_5 to AB_3-type with typical discharge capacities of 320–380 mAh g^{-1} are today used as active materials in commercial Ni–MH batteries [7–9]. However, they all contain expensive rare-earth elements and their mass capacity is limited by their high molecular weight. TiNi-based compounds are lighter and do not contain strategic rare-earth elements and therefore are promising compounds for next generation of Ni–MH batteries.

TiNi is however most known for its outstanding shape memory properties which are based on a reversible martensitic transformation. This transition is a diffusionless structural transformation between a high temperature phase with cubic structure (CsCl-type, $B2$ in *structure bericht* designation) and a low temperature phase with monoclinic structure ($B19'$). As a shape memory alloy, TiNi has lots of mechanical and biomedical applications: piping, actuators, stents… [10–12]. Much less attention has been paid to the fact that TiNi can absorb significant amount of hydrogen (1.4 hydrogen atoms per formula unit H f.u.$^{-1}$) at normal conditions of temperature and pressure [13]. Furthermore, TiNi exhibits electrochemical activity and good resistance to corrosion in alkaline media [14]. For all these reasons, the use of TiNi as active material in Ni–MH batteries can be envisaged.

Unfortunately, the discharge capacity of binary TiNi is rather low. Gutjahr et al. reported that 230 mAh g^{-1} can be obtained at slow kinetic regime while using two-phase TiNi–Ti_2Ni electrodes [15]. Interestingly, TiNi shows a good cycle life for more than 100 cycles. Chemical substitution in Ti or Ni sublattices can be effective to increase the discharge capacity. Thus, previous research in our group demonstrated that the hydrogenation capacity increases to 2.6 H f.u.$^{-1}$ for (Ti,Zr)Ni pseudobinary compounds leading to discharge capacities as high as 370 mAh g^{-1} at C/10 rate [16,17]. Unfortunately, the cycle-life of (Ti,Zr)Ni compounds is quite poor for the battery application.

In this study, the structural properties of Ti(Ni,Cu) intermetallic compounds (IMCs) as well as their solid–gas and electrochemical hydrogenation properties are investigated. We show that Cu substitution enhances the discharge capacity of binary TiNi up to 300 mAh g^{-1} at fast kinetic regime. Such a high capacity increase results from the destabilization of the hydride phase by the Cu substitution. These results demonstrate that the Ti(Ni,Cu) compounds, which do not contain costly rare-earth metals, are relevant materials for their use in commercial Ni–MH batteries.

2. Experimental methods

Cu substituted IMCs with nominal composition of $Ti_{1.01}Ni_{0.99-x}Cu_x$ ($x = 0, 0.1, 0.2, 0.3, 0.4$ and 0.5) were synthesized by induction melting in the form of alloy ingots. To ensure chemical homogeneity, the ingots were annealed at 1173 K for 4 weeks. Their chemical composition and microstructure were investigated by Electron Probe Micro Analysis (EPMA) with a Cameca SX-100 device. The martensitic transformation temperatures were determined by Differential Scanning Calorimetry (DSC) using a TA Q100 calorimeter in the range 200–400 K at the heating/cooling rate of 10 K min^{-1}. Samples were sealed in aluminum pans for this purpose. The crystal structure of IMCs and their hydrides was characterized by powder X-ray diffraction (PXRD) with a $\theta-\theta$ Bragg–Brentano diffractometer (D8 Bruker) using CuK_α radiation. For IMCs, diffraction data were obtained at RT and 473 K in powder samples. To produce the metallic powder, the samples were first embrittled by hydrogenation, next manually crushed to powder and then thermally desorbed by heating at 873 K under secondary vacuum. For hydrides, PXRD patterns were collected at RT.

Hydrogenation thermodynamics were characterized by Pressure Composition Isotherms (PCI) by the Sievert's method using home-made manometric benches. To speed up hydrogen absorption, the alloy ingots were first cut in to small pieces of ~1 mm in thickness by using a low speed diamond saw, etched with HF 10% solution for 30 s and rinsed with ethanol. Samples were activated for three absorption/desorption cycles before PCI acquisition. Absorption was carried out at $P_{H2} = 5$ MPa, $T = 423$ K and desorption at $T = 773$ K under primary vacuum.

Electrochemical properties were determined by galvanostatic cycling at RT in one-compartment cell. Negative working electrodes (typical mass 300 mg) were made of Ti(Ni,Cu) powders sieved under 63 μm and mixed with conductive black carbon and polytetraflutoethylene (PTFE) in 90:5:5 weight ratio. This mixture was spread out in sheets of 0.25 mm thick and compressed onto a Ni current collector. A positive $NiOOH/Ni(OH)_2$ electrode was used as the counter electrode and the potential was measured versus a Hg/HgO reference electrode (Hg/HgO vs. SHE = 0.098 V). A poly-amide sheet was placed between the positive and negative electrode as a separator to avoid the electrical shortcuts. 6 M KOH aqueous solution was used as electrolyte both in the electrochemical cell and in the reference electrode to avoid OH^- concentration gradients. The galvanostatic cycling was performed at the rate of C/10 (full capacity C in 10 h) with a cutoff potential of −0.7 V vs. Hg/HgO. Electrochemical isotherms were obtained at RT by the Galvanostatic Intermittent Titration Technique (GITT). For selected electrodes, high-rate capability studies were also carried out by galvanostatic charging at C/20 regime and subsequent discharge from 5D to D/20 rate.

To better understand the effect of Cu substitution on the electrochemical properties of TiNi, structural transformations of TiNi and $TiNi_{0.8}Cu_{0.2}$ compounds were characterized during electrochemical deuteration by *in-situ* Neutron Powder Diffraction (NPD). The composite electrodes were made from ~3.5 g of intermetallic powder using the same procedure as described before. The electrode sheets, about 1.5 mm in thickness, were rolled up on themselves to form cylinder of about 50 mm height and 10 mm diameter. The working electrode was placed between inner and outer cylindrical counter-electrode made of nickel, with silica sheaths as separators on each side of the working electrode. The working electrode was introduced in a specially designed silica cell [18] filled with electrolyte solution (5.5 M $NaOD/D_2O$) and equipped with $Cd/Cd(OD)_2$ reference electrode ($Cd(OH)_2/Cd$ vs. SHE = −0.809 V). The electrodes were charged at C/10 and discharged at D/10 rate with a cutoff potential of 0.5 V vs. $Cd(OH)_2/Cd$ otherwise specified. NPD data have been recorded at RT and ambient pressure with the High Resolution Powder Diffractometer for Thermal Neutrons (HRPT) in high sensitive mode at SINQ-PSI in Switzerland. The patterns were recorded by batch of 8 varying the detector angle by step of 0.15. Typical time acquisition was 225 s per pattern. The eight patterns were finally combined in one signal file leading to a time resolution of about 1800 s for each diffraction measurement. The diffraction patterns were sequentially refined by using the Rietveld method using the Fullprof software [19].

All electrochemical experiments were computer monitored using a VMP3 galvanostat from Biologic. Before running the experiments, electrochemical cells were pumped under primary vacuum in order to impregnate the working electrode with the electrolyte and to remove any gaseous molecules trapped in the electrode.