

PRODUCTION OF Ti-Zr-Ni ALLOYS BY POWDER METALLURGY FOR NICKEL METAL HYDRIDE BATTERIES

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ABSTRACT

The AB₂ alloys based Ti_{0.9}Zr_{0.1}Ni₂ and Zr_{0.9}Ti_{0.1}Ni₂ hydrogen storage alloys were prepared by powder metallurgy, using high speed planetary ball milling with speed of 200 rpm during 120 min. The samples were sintering at 1273K during 120 minutes under high vacuum. This alloy was used as negative electrode of nickel metal hydride batteries and the effects of the microstructure and electrochemical performances were investigated. The anode was prepared using a mixture of the alloy with carbon black and polytetrafluoroethylene (PTFE) used as a binder. Electrochemical measurements were performed in a standard tri-electrode system consisting of a working electrode (negative electrode), a platinum wire counter electrode and an Hg/HgO reference electrode. The electrolyte was 6 M KOH aqueous solution. Microstructure and phase composition of samples were investigated employing scanning electron microscopy (SEM) and X-ray diffraction (XRD).

Keywords: Hydrogen storage alloys, AB₂ alloys, Ni-MH batteries.

INTRODUCTION

Many hydrogen storage alloys have been used as negative electrode materials of rechargeable alkaline Ni–MH batteries^(1,2). At present, it is an important task to search for a new hydrogen storage alloy with a high discharge capacity for nickel metal hydride batteries.

Among all the alloys studied, AB₂-type hydrogen storage alloys have attracted the attention of investigators for their higher electrochemical capacities than that of the prevailing AB₅-type rare earth-based hydrogen storage alloys.

Substitution of Ni in Ti-based Laves phase alloys has been extensively studied in order to improve the electrochemical storage capacity because of the catalytic nature of Ni. The electrochemical studies of Zr-substituted AB₂ alloys reveal that the electrochemical storage capacity increases with increasing the amount of Zr. The presence of others elements in non-stoichiometric AB₂ alloys leads to the improvement of the storage properties thanks to the introduction of disorder in an unchanged C14 hexagonal structure presenting modified cell parameters^(3,4).

EXPERIMENTAL

The alloys of the nominal composition Ti_{0.9}Zr_{0.1}Ni₂ and Zr_{0.9}Ti_{0.1}Ni₂ were prepared by powder metallurgy. The purity of starting elemental metals was higher than 99%. In order to prepare the alloy the two following steps were adopted. In first step a binary Ti_{0.9}Zr_{0.1} (17.5%Zr + 82.5%Ti) and Zr_{0.9}Ti_{0.1} (5.5%Ti + 94.5%Zr) intermediary alloys were beforehand prepared by powder metallurgy using titanium and zirconium hydrogenated-powders.

The high energy planetary ball milling was using speed of 200 rpm for 120 minutes and milled powders were then cold isostatically pressed at 200 MPa, followed by sintering at 1273K (1000°C) for 120 minutes under high vacuum (10⁻³ Pa) and furnace cooled. The Tab.I shows the atomic and weight composition of Ti_{0.9}Zr_{0.1} and Zr_{0.9}Ti_{0.1} alloys.

Tab.I Atomic and weight composition of the Ti_{0.9}Zr_{0.1} and Zr_{0.9}Ti_{0.1} alloys.

Compositions		
Nominal	Atomic (at%)	Weight (%wt)
Ti _{0.9} Zr _{0.1}	Ti ₉₀ Zr ₁₀	82.5Ti-17.5Zr
Zr _{0.9} Ti _{0.1}	Zr ₉₀ Ti ₁₀	94.5Zr-5.5Ti

In order to prepare the ternaries alloys ($Ti_{0.9}Zr_{0.1}Ni_2$, $Zr_{0.9}Ti_{0.1}Ni_2$) the the following procedure was adopted. The binaries alloys ($Ti_{0.9}Zr_{0.1}$, $Zr_{0.9}Ti_{0.1}$) were hydrogenated (1 MPa H_2) and after milled with nickel powder (particle size less than $45\mu m$). The high energy planetary ball milling was utilized in the same conditions previously described. The Tab.II shows the atomic and weight composition studied in this work and the respective quantity of mass (g) utilized in 10 grams of milling.

Tab.II – Nominal composition, atomic and weight of the AB_2 alloys and quantity of mass (g) utilized in 10 grams of milling.

Composition			Mass powder (g)		
Nominal	Atomic (%at)	Weight (%wt)	$Ti_{0.9}Zr_{0.1}$	$Zr_{0.9}Ti_{0.1}$	Nickel
$Ti_{0.9}Zr_{0.1}Ni_2$	$Ti_{30}Zr_{3.3}Ni_{66.7}$	25.4Ti-5.4Zr-69.2Ni	3.07	-	6.93
$Zr_{0.9}Ti_{0.1}Ni_2$	$Zr_{30}Ti_{3.3}Ni_{66.7}$	40.2Zr-2.4Ti-57.4Ni	-	4.25	5.75

The negative electrode was prepared using 150 mg of the blended powder with carbon black (67%) and PTFE (33%). Three-electrode set-up cell was used in this study with a $Ni(OH)_2$ and a mercurous oxide (Hg/HgO) as the counter electrode and the reference electrodes, respectively. The electrolyte is 6M KOH solution.

The discharge capacity, activation and cycle stability of the alloy electrodes will be determined by automatic battery charge/discharge equipment. Each electrode will be charged with current density at 100 mA/g for 5h followed by a 10 min rest and then discharged at 50 mA/g to the cut-off potential of $-0.6V$ versus the Hg/HgO reference electrode.

Samples for the microstructure studies were prepared using conventional metallographic methods. The microstructures of the specimens were examined using a scanning electron microscope equipped with energy dispersive X-ray analysis facility. Powdered samples of the alloys ($<45\mu m$) were examined by X-ray diffraction (XRD). Identification of the various phases was carried out by comparison with standards of the ICDD data base and using the software Crystallographica Search-Match (CSM).

RESULTS AND DISCUSSION

Backscattered electron micrographs showing a general view of the $Ti_{0.9}Zr_{0.1}$ and $Zr_{0.9}Ti_{0.1}$ alloys are shown in Fig. 1. The chemical composition of the alloys is showed in Tab III.

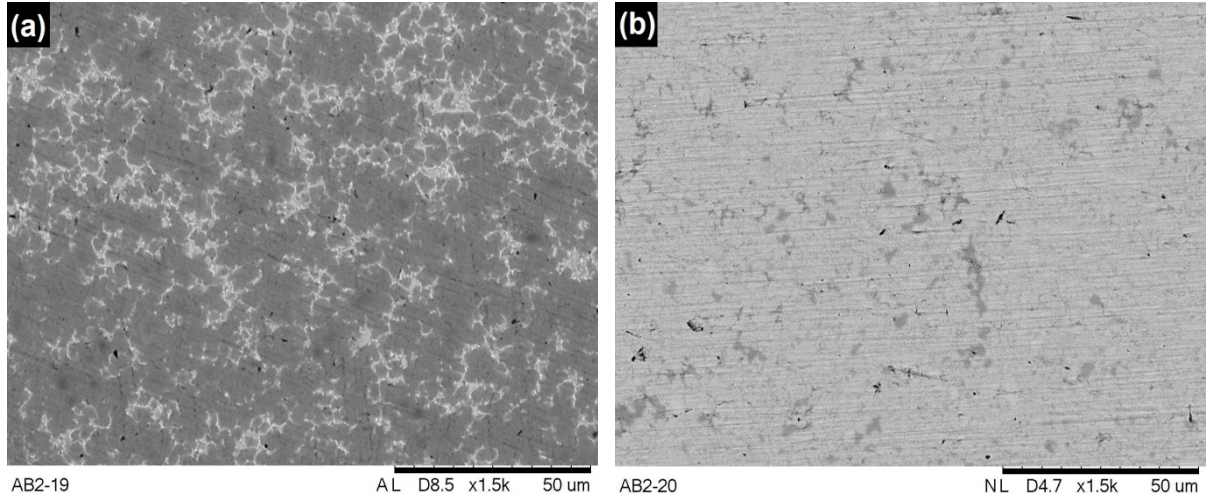


Fig. 1 - Backscattered electron micrograph of the (a) $Ti_{0.9}Zr_{0.1}$ and (b) $Zr_{0.9}Ti_{0.1}$ alloys, obtained by powder metallurgy.

Tab. III. Chemical composition determined by EDX of the $Ti_{0.9}Zr_{0.1}$ and $Zr_{0.9}Ti_{0.1}$ alloys.

Composition analyzed of alloy (at%)		
Alloys	Ti	Zr
$Ti_{0.9}Zr_{0.1}$	90.50	9.50
$Zr_{0.9}Ti_{0.1}$	10.10	89.90

Backscattered electron micrographs showing a general view of the $Ti_{0.9}Zr_{0.1}Ni_2$ and $Zr_{0.9}Ti_{0.1}Ni_2$ alloys are shown in Fig. 2. The chemical composition determined by EDX of the alloys is showed in Tab IV.

The $Ti_{0.9}Zr_{0.1}Ni_2$ and $Zr_{0.9}Ti_{0.1}Ni_2$ alloys are composed of two phases: the gray phase (G) and the dark gray phase (DG). The proportions of these two phases are showed in Tab. V – VI.

The Fig.3 shows XRD pattern of the $Ti_{0.9}Zr_{0.1}Ni_2$ and $Zr_{0.9}Ti_{0.1}Ni_2$ alloys.

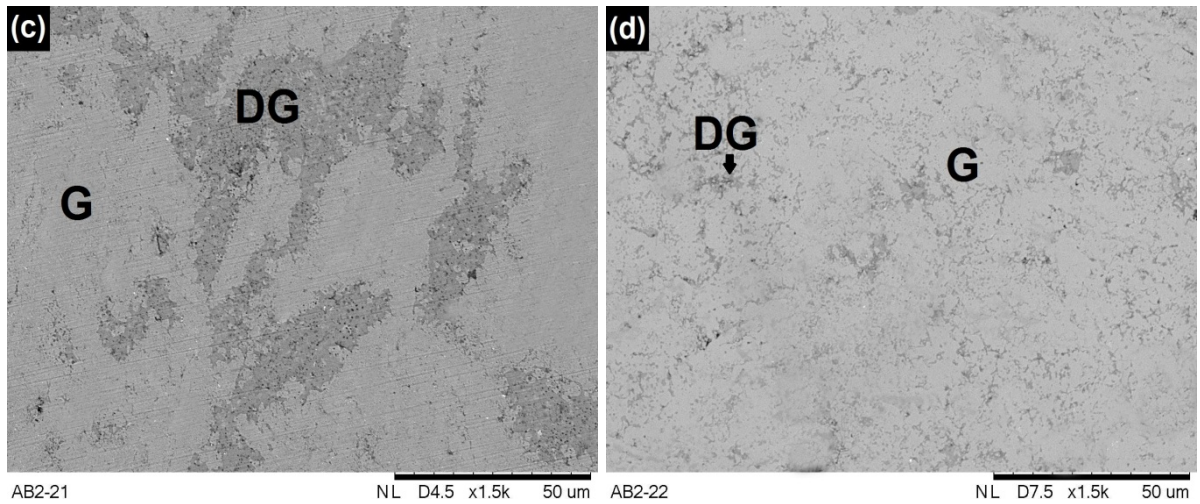


Fig. 2 - Backscattered electron micrograph of the (c) $Ti_{0.9}Zr_{0.1}Ni_2$ and (d) $Zr_{0.9}Ti_{0.1}Ni_2$ alloys, obtained by powder metallurgy.

Tab. IV. Chemical composition of the $Ti_{0.9}Zr_{0.1}Ni_2$ and $Zr_{0.9}Ti_{0.1}Ni_2$ alloys.

Composition analyzed of alloy (at%)			
Alloy	Ti	Zr	Ni
$Ti_{0.9}Zr_{0.1}Ni_2$	31.26	3.78	65.05
$Zr_{0.9}Ti_{0.1}Ni_2$	3.68	30.66	65.66

Tab. V. Composition determined by EDX of the G phase.

Composition analyzed composition of phase G (at%)			
Alloy	Ti	Zr	Ni
$Ti_{0.9}Zr_{0.1}Ni_2$	30.88	1.36	67.77
$Zr_{0.9}Ti_{0.1}Ni_2$	5.06	26.19	68.75

Tab. VI. Composition determined by EDX of the DG phase.

Composition analyzed composition of phase DG (at%)			
Alloy	Ti	Zr	Ni
$Ti_{0.9}Zr_{0.1}Ni_2$	52.80	4.48	42.71
$Zr_{0.9}Ti_{0.1}Ni_2$	5.00	62.52	32.49

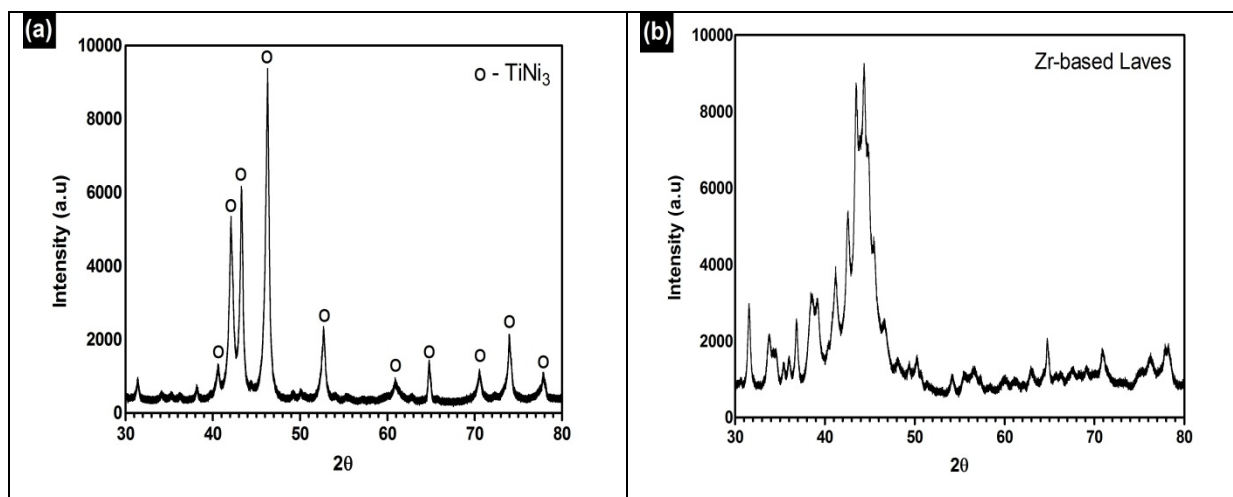


Fig 3 – XRD Pattern of the (a) $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Ni}_2$ and (b) $\text{Zr}_{0.9}\text{Ti}_{0.1}\text{Ni}_2$ alloys.

According with Yu et al⁽⁵⁾. X-ray diffraction, scanning electron microscopy and energy-dispersive X-ray analysis tests showed that the as-cast Zr-based Laves phase alloy consisted of at least eight phases. The major cubic C15-type Laves phase coexisted with the hexagonal C14-type Laves phase, orthorhombic $\text{Zr}_7\text{Ni}_{10}$ phase, tetragonal $\text{Zr}_9\text{Ni}_{11}$ phase, tetragonal ZrNi_2 and a few other phases. X-ray photoelectron spectroscopy proved that Zr and Mn were richer in the outer layer of the Zr-based Laves phase hydride electrode; Ni and Cr were deficient on the surface of the electrode. After 540 charging-discharging cycles, the discharge capacities of the Zr-based Laves phase hydride electrodes decreased by 20–30%. This was mainly caused by the formation of oxides at the surface of the electrodes.

The first ten cycles and maximum discharge capacity of the negative electrodes prepared using the crushed $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Ni}_2$ and $\text{Zr}_{0.9}\text{Ti}_{0.1}\text{Ni}_2$ alloys are shown in Fig.4 (a) and (b), respectively.

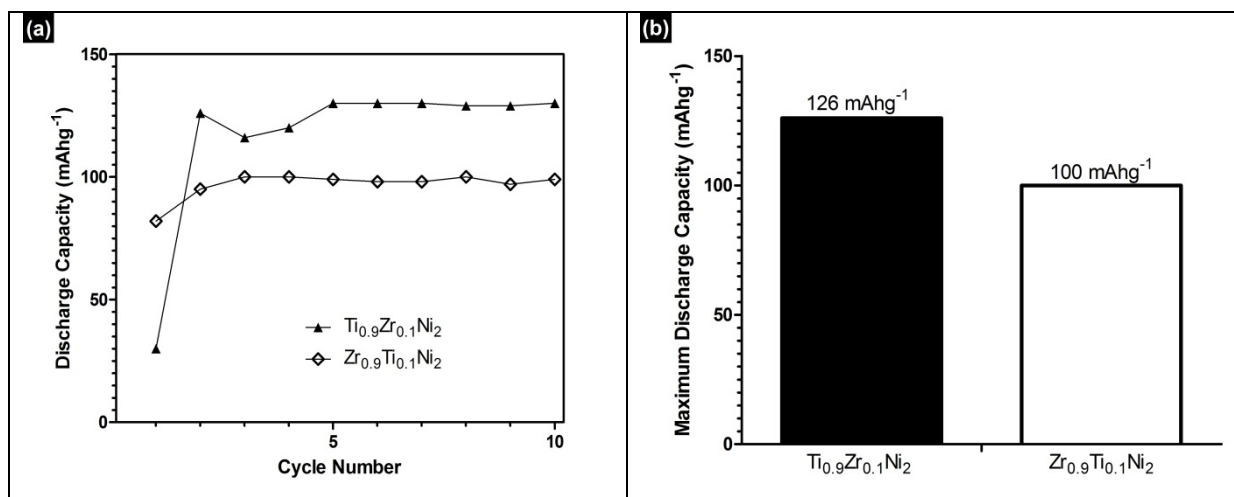


Fig. 4 (a) – First ten cycle number of negative electrode and (b) maximum discharge capacity of the alloys.

The best performance obtained was Ti_{0.9}Zr_{0.1}Ni₂ alloy with maximum discharge capacity of 126 mAhg⁻¹. The Zr_{0.9}Ti_{0.1}Ni₂ alloy showed less maximum discharge capacity (100 mAhg⁻¹). This result could be attribute increase of oxidation due a Zr-based Laves found in his alloy.

CONCLUSION

The two AB₂ alloys obtained a gray phase (G) and a dark gray phase (DG), but the compositions of these phases showed different. The XRD analysis showed presence of the TiNi₃ phase for Ti_{0.9}Zr_{0.1}Ni₂ alloy and Zr-based laves phase for Zr_{0.9}Ti_{0.1}Ni₂ alloy.

The Ti_{0.9}Zr_{0.1}Ni₂ alloy showed the best maximum discharge capacity (126 mAhg⁻¹).

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