

MICROSTRUCTURE AND ELECTROCHEMICAL PROPERTIES OF Ti-Nb-Zr-Ni ALLOY PRODUCED BY POWDER METTALURGY

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ABSTRACT

Powder metallurgy is utilized on the production of Ti-Nb-Zr alloys, making it possible to obtain structures with porous surface as result. Other advantages of powder metallurgy include better surface finish and better microstructural homogeneity. In this present work a study to produce AB₂ type-alloy with composition (TiNbZr)Ni₂ by powder metallurgy was realized. Ti-13Nb-13Zr (%wt) correspond to A alloy component and nickel to B. Ti-Nb-Zr-Ni alloy using was prepared via powder metallurgy, using high speed planetary ball milling with speed of 200 rpm during 120 minutes and sintering at 1273K during 600 minutes under high vacuum.

Keywords: Hydrogen storage alloys, Metal hydrides, Microstructures, Nickel metal hydride batteries.

INTRODUCTION

Hydrogen has been used as a pulverizing agent for rare earth-transition metals alloys due to its extremely high diffusion rate at low and high temperatures. Recently, Ti-13Nb-13Zr alloy has been developed and classified as totally biocompatible. This alloy shows low modulus of elasticity and high mechanical properties⁽¹⁾. Recent titanium

alloys used for biomedical applications contain a large amount of alloying elements with higher melting temperatures that is more difficult to obtain than traditional methods. In these cases powder metallurgy and hydrogenation of materials is advantageous, obtaining homogeneous alloys by making use of temperatures below melting temperature of materials⁽²⁾.

The alloys based AB₅ (LaNi₅) hydrogen storage alloy is the best choice for metal hydride (MH) electrode material used in nickel metal hydride (Ni/MH) batteries⁽³⁾. However, the limited discharge capacity shown that an alternative for new materials and process to obtain this alloys. The AB₂ alloys can be promising candidates.

In this study, AB₂ type alloys were produced by powder metallurgy. The Ti-13Nb-13Zr alloy and nickel powder was used to produce AB₂ alloy for production negative electrode for nickel metal hydride batteries.

EXPERIMENTAL

The Tab.I shown the atomic and weight composition of the (TiNbZr)Ni₂ alloy studied in this work.

Tab.I - Atomic and weight composition of the (TiNbZr)Ni₂ alloy.

Atomic composition (at%)	Weight composition (%wt)
Ti _{28.2} Zr _{2.6} Nb _{2.6} Ni _{66.6}	23.4Ti-4.2Zr-4.2Nb-68.2Ni

In order to prepare the alloy the two following methods was adopted. First method the Ti-13Nb-13Zr hydrogenated-alloy obtained in previous work⁽¹⁾ was crushed and milled with nickel powder. Second method titanium (Ti), niobium (Nb) and zirconium (Zr) hydrogenated-powders were milled with nickel powder (Ni). The particle size of the commercial nickel powder is less than 45µm. By the two methods the high energy planetary ball milling was using speed of 200 rpm for 120 minutes.

Milled powders were then cold isostatically pressed at 200 MPa, followed by sintering at 1273K (1000°C) for 600 minutes under high vacuum (10⁻³ Pa) and furnace cooled.

The Tab.II and III shown quantity of mass (g) used in first and second methods, respectively. To differentiate between the two methods the alloys were named AB₂-1 and AB₂-2.

Tab. II – Quantities of mass for production AB₂-1 alloy.

First Method	Ti-13Nb-13Zr alloy (g)	Nickel (g)	AB₂-1
	3.178	6.821	

Tab. III – Quantities of mass for production AB₂-2 alloy.

Second Method	Titanium (g)	Zirconium (g)	Niobium (g)	Nickel (g)	AB₂-2
	2.351	0.413	0.413	6.821	

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 µm) 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 and details of the AB₂-1 and AB₂-2 alloys are shown in Fig. 1. The chemical composition of the alloys is showed in Tab IV.

The AB₂-1 and AB₂-2 alloys are composed of two phases: the major phase (M) and a gray phase (G). The proportions of these two phases are showed in Tab. V - VI.

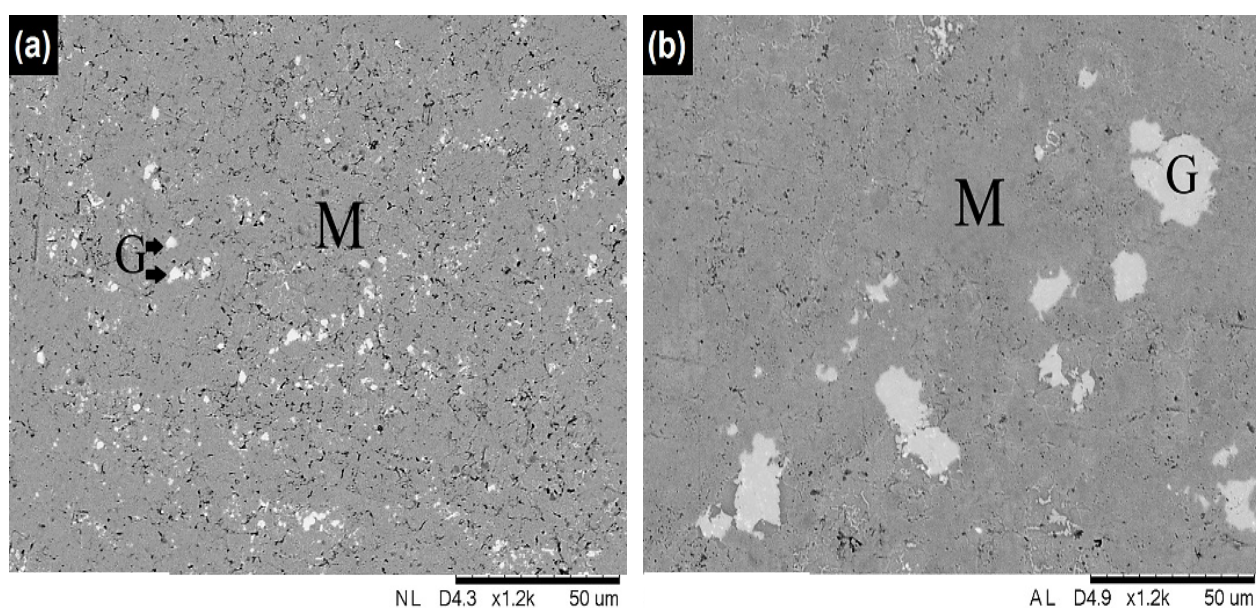


Fig. 1 – Backscattered electron micrograph of the (a) AB₂-1 and (b) AB₂-2 alloys.

Tab. IV. Chemical composition determined by EDX at the alloys.

Composition analyzed of alloy (at%)				
CODE	Ti	Zr	Nb	Ni
AB ₂ -1	28.02	2.76	2.60	66.61
AB ₂ -2	28.69	2.53	2.62	66.15

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

Composition analyzed composition of phase M (at%)

CODE	Ti	Zr	Nb	Ni
AB ₂ -1	26.95	1.47	2.10	69.48
AB ₂ -2	26.00	1.86	1.08	71.06

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

Composition analyzed composition of phase G (at%)				
CODE	Ti	Zr	Nb	Ni
AB ₂ -1	30.17	2.95	13.18	53.69
AB ₂ -2	40.89	1.55	11.29	46.36

The SEM analyses showed that gray phase is larger in AB₂-2 alloys than AB₂-1 alloy. The compositions of the alloys (Tab IV) showed similar results for two methods of fabrications compared com a Tab I (theoretical values). For the two methods a significant quantity of porous was found.

The EDX analyses showed differences between M and G phases. The gray phase showed a major area and large quantity of this phase in AB₂-2 alloy could be explain due second method of fabrication of this alloys was utilized separated elements (Ti, Nb, Zr, Ni).

X-ray diffraction patterns of the AB₂-1 and AB₂-2 alloys are shown in Fig 2. Just a one phase was identified: TiNi₃ (Space group: P63/mmc - PDF: 51-1169).

Comparing X-ray diffraction with SEM and EDX analyses, the TiNi₃ phase is shown M phase. Due small quantity of G phase compared with M phase is not possibility to find a diffraction peaks referring a G phase.

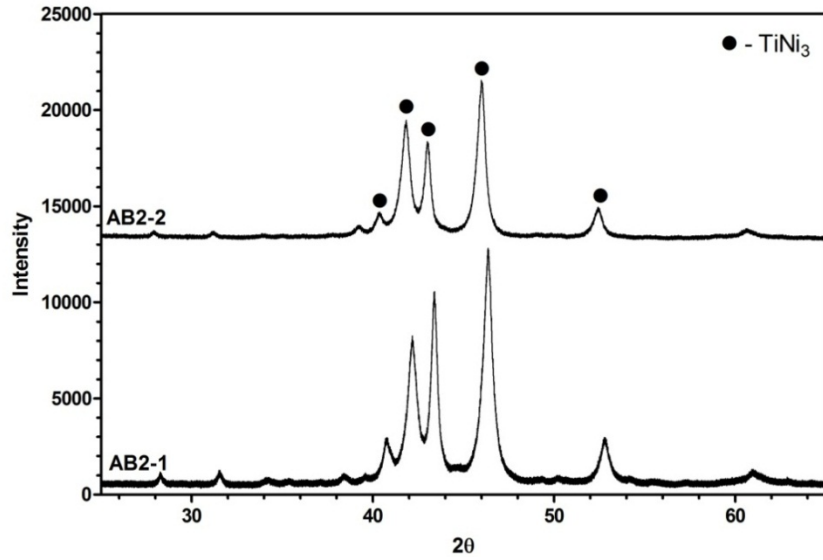
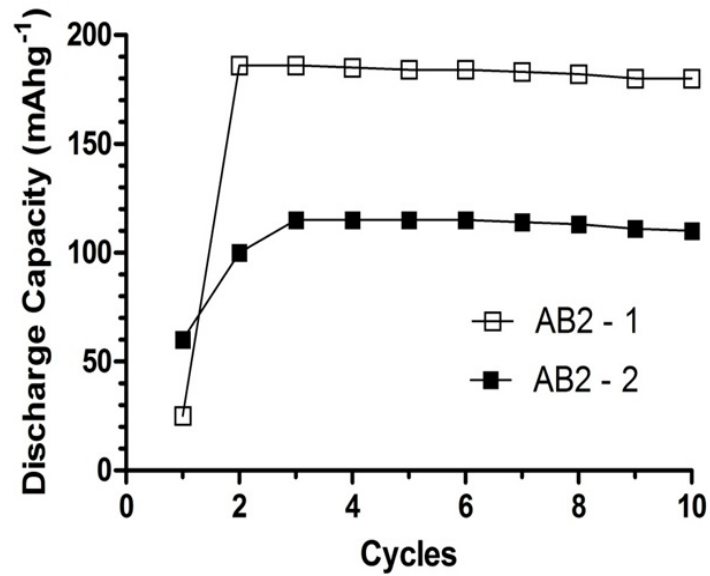


Fig 2 - X-ray diffraction of the AB₂-1 and AB₂-2 alloys.

The first ten cycles and maximum discharge capacity of the negative electrodes prepared using the crushed AB₂-1 and AB₂-2 alloys are shown in Fig. 3 (a) and (b), respectively.



(a)

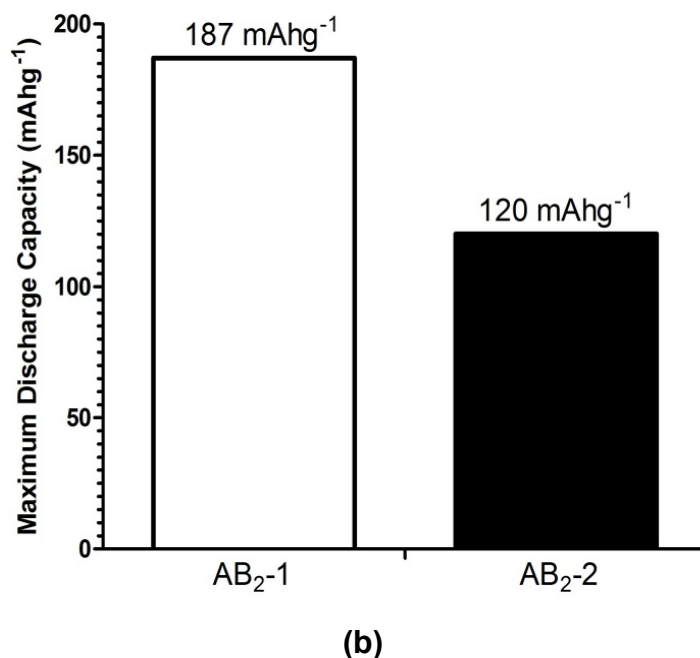


Fig. 3 (a) – Cycle life of negative electrode of the alloys, (b) Maximum discharge capacity of the alloys.

The best performance obtained was AB₂-1 alloy with maximum discharge capacity of 187mAhg⁻¹. The AB₂-2 alloy showed less maximum discharge capacity (120 mAhg⁻¹). This result could be attribute increase of gray phase due a separated milling of elements.

A discharge capacity of this alloys showed poor comparing with literature 250 mAhg⁻¹ (Ti_{0.25}V_{0.35}Cr_{0.10}Ni_{0.30}), it could be attributed an absence of other important elements in AB₂ alloys, for example a vanadium, manganese and chromium^(4, 5).

The influence of niobium in a microstructure and electrochemical performance of AB₅ alloys (LaNi₅) could be finding in a literature⁽⁶⁾. This paper showed influence of substitution of cobalt by niobium in a La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5-x}Nb_xNi_{3.8} alloy. Niobium might contribute decrease a

discharge capacity and change a microstructure forming a new phase with nickel.

The next important step is a study of increase sintering time and temperature. This study can be improve the alloy homogeneity (reduce gray phase) reflecting to increase a performance of the alloy in a negative electrode.

CONCLUSION

The two methods of fabrication of AB₂ alloy obtained a matrix phase (M) and a gray phase (G), but in second method the gray phase is larger. Matrix phase showed to be a TiNi₃ and a gray phase a niobium concentrated.

The first method of fabrication (AB₂-1) of this kind of AB₂ alloy showed the best maximum discharge capacity (187mAhg⁻¹).

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