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MICROSTRUCTURE AND HYDROGEN ABSORPTION BEHAVIOR OF $Zr_{0.9}Ti_{0.1}Mn_{0.66}V_{0.46}Ni_{1.1}$ UNDER ELECTROCHEMICAL AND GASEOUS MEDIA CONDITIONS

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Abstract— **Rechargeable alkaline batteries of nickel-metal hydride have been widely studied due to the interest in replacing the cadmium electrode by metal hydride electrodes of low or null environmental impact. Recent developments include Laves phases based on $ZrCr_2$ with multiple substitutions to improve electrode performance. In this work, results are presented on the electrochemical behavior of the $Zr_{0.9}Ti_{0.1}Mn_{0.66}V_{0.46}Ni_{1.1}$, its structural and morphologic characterization and its behavior under gaseous hydrogen absorption- desorption cycles. The pressure-composition-temperature (PCT) curves show a high hydrogen storage capacity (H/M ~ 3.4, where H/M = x is the number of H atoms per alloy formula unit in the metal hydride MH_x). It is also found a steep slope in the PCT isotherms, instead of a horizontal plateau corresponding to the two-phase equilibrium. Electrode activation was studied by voltammetric cycles, while the electrochemical capacity of hydrogen absorption was determined by galvanostatic measurements. For comparison, the $Zr_{0.9}Ti_{0.1}CrNi$ alloy was also studied. The discharge capacities found are about 330 mAh/g for both alloys, but the activation is achieved faster for $Zr_{0.9}Ti_{0.1}Mn_{0.66}V_{0.46}Ni_{1.1}$ than for $Zr_{0.9}Ti_{0.1}CrNi$.**

Keywords— **Batteries; metal hydrides; hydrogen storage; electrochemistry; over-stoichiometry.**

I. INTRODUCTION

In the last years there has been a large increase in the use of rechargeable alkaline batteries for domestic uses. The nickel-cadmium battery is among the most utilized batteries. Due to the toxicity of Cd, the necessity arises of replacing the Cd electrode by another one leading to no environmental pollution.

Bearing this in mind and due to the demand of high performance energy sources, rechargeable batteries of Ni-metal hydride (Ni-MH_X) have been developed and commercialized. With these batteries, the following characteristics are looked for: high energy density, high power density without loss of rate capability, long charge-discharge cycle life and better environmental compatibility.

This type of batteries uses as negative electrode a hydrogen storage alloy, in which the hydrogen atoms are incorporated to the solid by the reversible formation of a hydrided phase. In current commercial batteries the utilized alloys are of the AB_5 type, based on the compound $LaNi_5$ with variations in the composition.

Recently, the interest in the study of Zr based Laves phase metal hydrides, i.e. AB_2 type intermetallic compounds, where A = Zr and B = Ni, V, Mn, Cr, etc., has increased due to their higher hydrogen storage capacity and, hence, higher electric charge of the battery. However, in the initially studied alloys, the power density was not comparable to the AB_5 type. This situation encouraged research to optimize their composition (Kim *et al.*, 1998a, b; Klein *et al.,* 1998).

The activation of the alloy plays a fundamental role in the absorption electrodic process, since it defines the reaction rate of the hydrogen with the metal and the incorporation to its structure. During activation, several different processes occur (Sastri *et al.,* 1998; Anani *et al.,* 1994; Visintin *et al.,* 1996), such as: i) reduction of surface oxides that interfere with hydrogen, ii) reduction of particle size due to cracks produced by the volume increase, iii) changes in the chemical composition and/ or surface structure of the metal.

In this work, a technique is presented allowing for the acceleration of activation rate by the utilization of cyclic voltammetry in combination with charge-discharge galvanostatic cycles, which makes possible the determination of the real hydrogen storage capacity of the electrodes. This technique was applied to the $Zr_{0.9}Ti_{0.1}Mn_{0.66}V_{0.46}Ni_{1.1}$ alloy of over-stoichiometric composition, equivalent to the one optimized by Kim *et al.* (1998a). Furthermore, a characterization of this alloy is carried out from the metallurgical point of view and from the behavior of hydrogen absorption in gaseous phase.

The same electrochemical technique was also ap-