

## ELECTROCHEMICAL CHARACTERIZATION OF $Zr_{0.9}Ti_{0.1}Mn_{0.66}V_{0.46}Ni_{1.1}$ ALLOYS FOR BATTERY APPLICATIONS

W.E. TRIACA<sup>†</sup>, H.A. PERETTI<sup>‡</sup>, H.L. CORSO<sup>‡</sup>, A. BONESI<sup>†</sup> AND A. VISINTIN<sup>†</sup>

<sup>†</sup> Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas, Facultad de Ciencias Exactas, UNLP, Suc. 4, C.C. 16, (1900) La Plata, Argentina.

<sup>‡</sup> Centro Atómico Bariloche, CNEA, C.C. 439, (8400) San Carlos de Bariloche, Argentina.

### INTRODUCTION

The interest in the study of Zr-based Laves phase metal hydrides, i.e.  $AB_2$  type intermetallic compounds, where  $A = Zr$  and  $B = Ni, V, Mn, Cr, \text{etc.}$ , has increased because of their high hydrogen storage capacity is very attractive for battery applications (1). The activation of the alloy plays a fundamental role in the hydrogen absorption process, since it defines the reaction velocity of the hydrogen with the metal and the incorporation to its structure (2). In this work, the hydrogen absorption characteristics and the electrochemical properties of  $Zr_{0.9}Ti_{0.1}Mn_{0.66}V_{0.46}Ni_{1.1}$  alloys are studied in order to determine their possible application as the negative electrode in nickel / metal hydride batteries.

### EXPERIMENTAL

The alloy samples were prepared by arc melting adequate proportions of the constituent elements of purity better than 3N, under high purity inert atmosphere in a cooled copper hearth. The obtained alloys of the  $AB_2$  type, of compositions  $Zr_{0.9}Ti_{0.1}CrNi$  and  $Zr_{0.9}Ti_{0.1}Mn_{0.66}V_{0.46}Ni_{1.1}$ , were used without any subsequent thermal treatment. The electrodes were prepared by cold pressure of the powders using equal parts by weight of alloy (particle size  $\leq 105 \mu m$ ) and of Teflon treated carbon (Vulcan XC-72). A Ni wire was used as current collector. The electrochemical measurements were carried out by using a 7 M KOH solution at 30 °C and a Hg/HgO reference electrode.

The behavior of the alloy for hydrogen absorption from the gas phase was investigated by measuring pressure- composition- temperature (PCT) curves by means of the classical volumetric technique, using a Sievert type apparatus .

### RESULTS

The activation process of the  $AB_2$  type alloys for the hydrogen absorption in a KOH solution at 30 °C was evaluated by using the cyclic voltammetry technique. By comparing the alloys of different compositions, as shown in Fig. 1, it is observed that the  $Zr_{0.9}Ti_{0.1}Mn_{0.66}V_{0.46}Ni_{1.1}$  alloy reaches its maximum capacity after 25 voltammetric cycles, whereas the  $Zr_{0.9}Ti_{0.1}CrNi$  alloy requires 175 cycles.

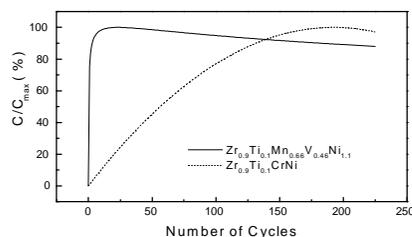


Fig. 1. Capacity vs. number of voltammetric cycle. v: 1mV/s; E(l): -1.4 V; E(u): -0.4 V. 7M KOH, 30 °C.

On the other hand, from galvanostatic charge – discharge cycling measurements charge storage capacities of 324 mAh/g for  $Zr_{0.9}Ti_{0.1}Mn_{0.66}V_{0.46}Ni_{1.1}$  and of 330 mAh/g for  $Zr_{0.9}Ti_{0.1}CrNi$  were obtained.

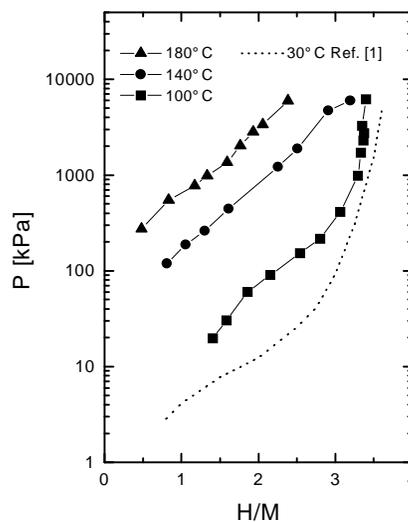


Fig. 2 PCT curves of  $Zr_{0.9}Ti_{0.1}Mn_{0.66}V_{0.46}Ni_{1.1}$  at different temperatures.

The PCT curves obtained at 100, 140 and 180 °C are shown in Fig. 2. As can be seen, the measured isotherms present a steep slope with a slight plateau tendency similar to that reported in (1) for the same alloy at 30 °C. This feature can be attributed to the microsegregation of alloying elements occurring during solidification, since in both cases the alloys have not been subjected to homogenizing treatments after melting. Saturation for the isotherm at 100 °C occurs at hydrogen pressures above 2000 kPa for a value of  $H/M \approx 3.4$ , whereas at 500 kPa the  $H/M$  ratio is 3.2 .

### DISCUSSION

The  $Zr_{0.9}Ti_{0.1}Mn_{0.66}V_{0.46}Ni_{1.1}$  and  $Zr_{0.9}Ti_{0.1}CrNi$  alloys present charge storage capacity values practically of the same order. However, the activation of the former is achieved faster, indicating that the substitution of Cr by Mn and V leads to an acceleration of the activation processes, possibly due to the formation of oxides that can be reduced more easily. In this respect, preliminary experiments show that noble metal coatings also accelerate the activation process and increase the rate capability of these alloys. The fact that the measured charge storage capacity for the  $Zr_{0.9}Ti_{0.1}Mn_{0.66}V_{0.46}Ni_{1.1}$  alloy is smaller than that reported in (1) (392 mAh/g), can be ascribed to small differences in the alloy composition, since its behavior is very sensitive to small variations of alloying element contents.

### ACKNOWLEDGMENTS

This work was supported by the Consejo Nacional de Investigaciones Científicas y Técnicas of Argentina, the Comisión de Investigaciones Científicas of Pcia. Bs. As. and the Agencia Nacional de Promoción Científica y Tecnológica.

### REFERENCES

- 1-D. M. Kim, S. W. Jeon and J. Y. Lee, J. Alloys Compd., **279**, 209 (1998).
- 2- A. Anani., A. Visintin, K. Petrov, S. Srinivasan, J. Reilly, J. Johnson, R. Schwarz and P. Desch, J. Power Sources, **47**, 261 (1994).