The study of H-absorption-desorption process in Ni$_{67}$-$X$M$_X$Zr$_{33}$ glassy alloys monitored by in situ resistance measurements

S. Balla$^1$ B. Vehovszky$^1$, A. Bárdos$^1$ and M. Kovačková$^2$

$^1$Department of Vehicle Manufacturing and Repairing, BUTE, Budapest H-1111, Bertalan Lajos utca 2. Hungary

$^2$Department of Physics, Faculty of Electrical Engineering and Informatics, Technical University of Košice, Park Komenského 2, 042 00 Košice, Slovakia

E-mail: balla@kgtt.bme.hu

Abstract. The catalytic potency and the existence of irreversible H-sorption induced by the addition of various 3d transition elements and noble metals in Ni$_{67}$Zr$_{33}$ glassy alloy are investigated. The cyclic H-absorption and desorption are monitored by in situ resistance measurements. While the periods of H-absorption and desorption are significantly shortened in the case of Pd and Cr addition, this effect is not detectable in the case Pt or Cu alloying. The resulting resistance increase due to H-absorption is highly composition specific, and no reasonable explanation was found for the correlation between the magnitude of resistance change and the chemical properties of alloying element. Opposite to the variety of catalytic effects, the irreversible H-trapping can be detected in each alloy by the resistance measurements, which indicates the dominant role of Zr host metal in this phenomenon.

1. Introduction

The characteristics of H-absorption in amorphous alloys are inherited from the chemical properties of host metal and, from the absence of topological long range order in the absorber. The metallic glasses, in which the host metal exhibits positive solution enthalpy of H-solution ($\Delta H > 0$), the interaction between electronic structure of metallic host (several 3d transition metals like Fe, Ni, Co, Cu) and the dissolved H atoms is negligible. Due to the weakness of this interaction, the H site occupation manifests itself mainly in the stress-sensitive properties, e.g. mechanical brittleness, or the stress sensitive magnetic properties, i.e., coercivity ($H_c$), magnetic anisotropy ($K_u$), etc. [1, 2]. Another important feature of this solution is the predominant reversible change of these properties during the spontaneous H-depletion [3, 4].

In contrast, those of metallic glasses in which (at least) one component is hydride-forming ($\Delta H< 0$), the quantity of dissolved H can be high, approaching the typical H/M values in the traditional crystalline storage alloys. The property changes are partially irreversible under the same state variables, though the well known isotherm plateau (characteristic for the PCT curves in crystalline H-absorbers) is absent [5]. The interaction between hydrogen atoms and the electronic band structure of the metallic absorber is detected by the UPS measurement [6]. In spite of the detailed investigations of H-absorption in the Zr-based glasses the available results restricts mainly to electrolytic saturation processes and, only little information is available about the catalytic phenomena and the degree of
irreversibility of hydrogen trapping and the related property changes in these glasses especially when the H-absorption is taking place during solid–gas reactions.

In this paper the role of additive elements in Ni$_{67-x}$M$_x$Zr$_{33}$ (M=Pt, Pd, Cr; x=0, 3, 5) alloys is studied from the point of view of the above mentioned properties of Ni$_{67}$Zr$_{33}$ based glasses. The cyclic H-saturation was performed in a gas phase, and the H-charging and discharging process were monitored by in situ resistance measurements.

2. Experimental

The alloys were prepared by induction melting in cold crucible. Pieces from ingots were liquid-quenched into ribbon form, using traditional melt-spinning in inert atmosphere. The glassy state was confirmed by X-ray diffraction. Subsequently, the ribbons were chemically analyzed using atomic absorption. Prior to the charging the samples surfaces were abraded and, etched for a few minutes in 4% HF solution, in order to remove the surface oxide contaminations. Measurements were carried out in a high-pressure chamber in which the sample holder was placed together with the samples. The details of in-situ resistance measurements have been described in Refs. [7-9].

3. Results and discussion

The catalytic potency of Pd, Pt, additives on the rate of H-absorption can be compared in the Fig.1., where the time-dependence of cyclic charging-discharging is monitored by in situ resistance measurements on binary Ni$_{67}$Zr$_{33}$, Ni$_{67}$Pd$_3$Zr$_{33}$, and Ni$_{64}$Pt$_3$Zr$_{33}$ glasses. Though the concentration of Pt or Pd additives is very low, the shapes of charging-discharging curves exhibit significant differences. Both the charging and discharging periods are significantly shortened in the case of Ni$_{67}$Pd$_3$Zr$_{33}$, compared to the Ni$_{67}$Zr$_{33}$, and Ni$_{64}$Pt$_3$Zr$_{33}$ glasses.
The common features of the curves are:

- Resistance change cannot be detected when the samples are heated from room temperature to 100 °C, (which is the temperature of H-absorption), which is in agreement with the known low temperature coefficient of resistivity of glassy alloys [8]. This fact does confirm that all of the observed changes in the $R/R_0$ during H-charging or discharging experiments arise solely from the incorporation or depletion of H atoms in the samples. As it is reflected in the shape of curves, the saturation H-content is obtained in all samples within a few minutes at 100 °C. The significant shortening in the saturation time in Ni$_{67}$Pd$_3$Zr$_{33}$ indicates the well known catalytic effect of the dissolved Pd. At the same time, it is surprising, that such catalytic effect of Pt addition cannot be detected although it was expected due to the well known catalytic potency of metallic Pt in similar hydrogenation-reactions.

- The saturation H-content (determined by direct mass measurements) is nearly the same for all samples. In spite of this, the slopes and the saturation values for $R/R_0$ curves differ strongly in the investigated alloys (sat. $R/R_0$ is lower for Ni$_{65}$Pd$_3$Zr$_{33}$, and Ni$_{65}$Pt$_3$Zr$_{33}$ samples), which clearly shows the non-existence of universal relation between the $R/R_0$ increase and the corresponding H-content.

- The shape of individual curves seems to be independent from the individual chemical affinities between the hydrogen and the Pd or Pt elements (both of the H solubility and the enthalpy of hydride formation differ significantly in these metals) [9]. The differences between the $R/R_0$ at saturation are conserved even at various ambient H-pressures (10 atm) and temperatures. It means that the magnitude of H-induced resistance increase is composition-specific property of the investigated alloys and seems to depend on the change in electron density of states near the Fermi surface of alloys, which are influenced by the H-absorption. As the formation of H-Zr bonds are dominant in the process the contribution of conduction electrons arising from the Zr atoms decreases in the valence band [10].

Another important observation is the partial irreversibility of $R/R_0$ at a constant temperature, which is the lowest for Ni$_{65}$Pd$_3$Zr$_{33}$ and the highest for the Ni$_{67}$Zr$_{33}$, indicating that H-trapping at a constant temperature is more pronounced due to the higher portion of Zr-H bonds. This is a common feature of the H-storage alloy-systems.

![Fig.2. The change of $R/R_0$ during the H-absorption-desorption cycles in Ni$_{62}$Cr$_2$Zr$_{33}$ and Ni$_{62}$Cu$_6$Zr$_{33}$ glasses](image-url)
Similar R/R₀ curves can be compared in Fig.2 for ternary alloys, in which the Ni is partially replaced by Cr or Cu. The Zr-content (which is responsible for the H-absorption), is the same as in the previous alloys. The chemical affinity between H and the Cr or Cu is low (ΔH of solution is much lower, than that for Pd [11]). In spite of this, the characteristic time of H-absorption-desorption cycle, hence the shape of R/R₀ curves is similar to that for Ni₆₇Pd₃₃Zr₃₃ alloy.

There is no complete interpretation of the variety of pressure and temperature dependence of R/R₀ in the investigated alloys. Nevertheless, the definite catalytic effect caused by the Pd and Cr addition was confirmed by several experiments.

4. Summary

- The relative resistance change caused by the H-absorption and desorption is a useful method for monitoring the process of H-absorption and desorption in various glassy alloys. However, the shape of R/R₀ curves is strongly composition dependent, and there is no universal explanation of this variety.
- The definite catalytic effect of Pd and Cr addition was found both in the H-absorption and desorption processes.
- The irreversible part of H-absorption can be detected in each alloy during the in situ resistance measurements. In spite of the identical Zr-content the degree of irreversibility is more pronounced in the case of binary Ni₆₇Zr₃₃ glass.

Acknowledgements
This work has been supported by the Hungarian Fund (OTKA) through grant No. T 046239 and No. T 048708.

References

[1] Novák, L., A. Lovas, L. F. Kiss: J. Appl. Physics, 98, 1-5 (2005)
[2] Novák, L., K. Bán, J. Kováč, A. Lovas, Journal of Magn. and Magn. Mat., Elsevier, Vol. 304, Issue 2, (2006) pp.: 669-671
[3] Mohanta, O., A. Mitra, I. Chattoraj, J. Magn. Magn. Mater.266 (2003) 296-301
[4] K. Bán, A. Lovas, L. Novák, K. Csach, Czechoslovak: of Phys. 54 Suppl. D 137-140, (2004)
[5] A. J. Maeland: Rapidly Quenched Metals, eds. S. Steeb, H. Warlimont, Elsevier Science Publishers B.V. (1985) pp. 1507-1514
[6] R. Zehringer, P. Oelhafen, H.J. Güntherodt, Mater. Sci. Eng 99, 253-256 (1988)
[7] J. Garaguly, A. Lovas, Á. Cziráki, M. Reybold, J. Takács, K. Wetzig: Mater Sci Eng. A 226-228, 938-942,(1997)
[8] Y. Yamada and K. Tanaka: Electrical resistivity change during hydrogen charging and subsequent heating in Ni–Zr alloy glasses, Transactions of the Japan Institute of Metals, Vol. 27, No. 6 (1986) pp. 409-415
[9] J. Tóth, I. Bakonyi, A. Lovas and K. Tompa: Electrical transport studies of glassy Zr-Ni Hydrides, J. Less-Comm. Metals, 155 (1989) pp. 185-191
[10] H. Jones, Rapid Solidification of Metals and Alloys, The Institution of Metallurgists, ISBN 0901-462-18-7, III.o.
[11] J. D. Fast: Interaction of Metals and Gases, Vol.1 Thermodynamics and Phase relations, Philips Technical Library, 1965.pp.125
[12] G.Pető,I. Bakonyi, K.Tompa, É. Zsoldos,L. Guzczi, Solid State Communication 70 No7, 781-784, (1989)
[13] Y. Fukai, The Metal-Hydrogen System, (p.105) Springer Verlag, 1992