ELSEVIER

Journal of Alloys and Compounds 253–254 (1997) 114–117

Journal of ALLOYS AND COMPOUNDS

Electrical resistance change during hydrogen charging and discharging in $Ni_{67-x}Cu_xZr_{33}$ glassy alloys

J. Garaguly[b,*], A. Lovas[a], K. Tompa[a], J. Takács[b]

[a] *Res. Inst. for Solid State Physics, Hun. Academy of Sci., H-1525 Budapest, POB 49, Hungary*
[b] *Dept. of Mech. Eng. Tech., Tech. Univ. of Budapest, H-1111 Budapest, Bertalan L. St. 2, Hungary*

Abstract

The hydrogen charging and discharging processes are investigated in $Ni_{67-x}Cu_xZr_{33}$ glassy alloys by in situ resistance measurements in order to clarify the surface and bulk contribution to the activation process. The process has been monitored by conventional DC method using a computer-controlled system, exposing the samples to hydrogen at pressure from 0.1–8.6 MPa at temperatures of 293 K and 393 K. The H-contents (H/M) were determined by weight and by pulse NMR measurements. The NMR data are obtained by the Carr–Purcell–Meiboom–Gill (CPMG) method. The charging is extremely long and the resulting H-distribution is inhomogenous during the first cycle, especially at 293 K. This fact shows the significance of the surface-activation during the H-uptake from the gas phase. The duration of the second saturation decreases significantly, and the resistance–time curves obtained: on two parallel samples are very similar. The saturation value for the normalized resistance (R/R_0) remains almost the same during several cycles. Increasing the temperature of the charging (393 K), the equilibrium value of the resistance decreases. The resistance of the samples at the end of the discharging process is always higher than before charging. This indicates the partial irreversibility of the H-absorption at constant temperature. This observation is correlated with the NMR results.

Keywords: Hydrogen charging–discharging; Resistance; Surface and volume activation

---

1. Introduction

The processes of H-absorption and desorption in glassy alloys are often monitored by the change in the electrical resistance. As the absorption proceeds, the resistance usually increases for alloys in which the solution enthalpy of hydrogen is negative. The negative enthalpy change arises mainly from the interaction between the conduction electrons of the metallic host and the dissolved H-atoms. The electron density of states near the Fermi level (which is mainly dominated by the Zr 4d electrons) is gradually decreased as a consequence of the increasing number of chemical bonds formed between the H 1s-electrons and Zr 4d electrons during the absorption [1,2]. The electrical resistance is not necessarily a monotonous function of the H-content [3], but for amorphous Ni–Zr alloys it is monotonous. This allows us to follow the absorption process by the resistance change, as is described in [4,5].

Ni–Zr glassy alloys are promising because of their relatively high reversible H-storage capacity. Besides, absorption and desorption takes place within a reasonable time-scale and temperature range in the case of the composition $Ni_{67}Zr_{33}$ [6].

Our aim is to clarify some of the details of the surface and bulk contribution. to the activation process during the H-absorption and repeated charging–discharging cycles. In addition, the in-situ resistance measurements are extended to the ternary $Ni_{67-x}Cu_xZr_{33}$ system.

2. Experimental details

The sample preparation (abrading or HF-treatment) and characterization as well as the arrangement of the resistance measurements (two parallel samples...) are described in [7]. The results on the time-dependence of the normalized resistance (R/R_0, where R_0 is the resistance of the samples before the first H-charging–H/M=0–) will also be presented there. In this paper R/R_0 values measured at different temperatures, exposing the samples to hydrogen in the pressure range of 0.1–8.6 MPa, are discussed. The values of R/R_0 are related to the H-content determined by weight change measurements and checked by NMR using the CPMG method [8].

---

[*] Corresponding author.

0925-8388/97/$17.00
PII S0925-8388(96)03061-7

3. Results and discussion

3.1. Sample homogeneity and the time-dependence of R/R_0 during the first saturation

A large difference was found between the time scales belonging to the first charging and the subsequent ones in all the investigated samples. (See Fig. 1.) This fact and the magnitude of the difference do not depend significantly on the applied surface pre-treatments. Another important feature of the first saturation is the macroscopically inhomogenous H-distribution, which is indicated by the different shapes (time-dependence) of the R/R_0 curves obtained on two parallel samples. This difference completely disappears during the second saturation, and the curves coincide (Fig. 1). The inhomogeneity also manifests itself in the mechanical properties. The absence of brittleness (which is characteristic of the sample after complete saturation) was found on macroscopic pieces of samples during mechanical attrition after the first saturation. The inhomogeneous H-distribution during the first saturation is also supported by thermopower measurements which are sensitive to the local inhomogenities [10]. One can suppose that inhomogeneity arises from the uncontrolled thickness of the residual oxide layer on the surface in spite of the applied mechanical or chemical surface treatment. It seems that the H-penetration preferentially takes place through the (recently not sufficiently characterized) cracks, or active places in the residual surface oxide layer. As a consequence of the volume expansion during the first saturation, the surface oxide layer is disintegrated and submicroscopic active channels through the surface layer are created. For the comparison of the main characteristics of the first and subsequent saturations, the time intervals (t_{30-99}), during which $(R-R_0)/R_0$ increases from 30–99% of the maximum value (see Fig. 1), are plotted versus the number of cycles in Fig. 2 for $Ni_{67}Zr_{33}$. The value of 30% is used because it can be reached within reasonable time during the discharging processes. This characteristic time interval decreases by at least an order of magnitude between the first and second cycle. The decrease is going on during the repeated cycles, but very slowly. However, the partial recovery of the surface oxide layer causes a transient increase in the saturation time as it can be seen in the 10th and 11th cycles. The cycling was interrupted here and the samples were exposed to air for 15 min.

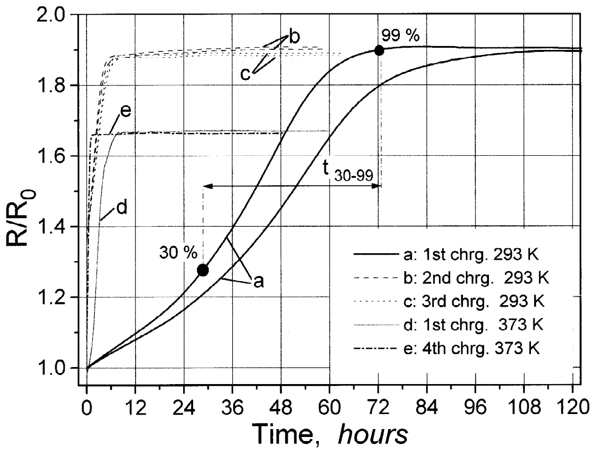

Fig. 1. Hydrogen saturation at 273 K and 373 K in $Ni_{67}Zr_{33}$ samples.

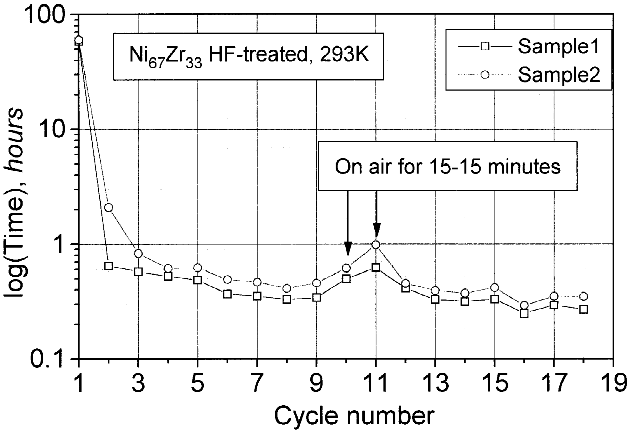

Fig. 2. Time interval $t_{30\text{-}99}$ versus cycle number.

3.2. The correlation between H/M and R/R_0

In order to avoid the errors arising from the sample inhomogeneity, the relation between H/M and R/R_0 was determined after the second saturation, for different degrees of the desorption. (See Fig. 3.) As the values of the H/M had been obtained after vacuum pumping the samples at 393 K, the validity of the reference value, R_0 so the adequate normalization) may be questionable because of the possible simultaneous structural relaxation of the samples. To eliminate this possible source of error, a long-time vacuum-heat treatment was carried out in order to detect the possible increase of the resistance without dissolved H. It was found that there is no detectable resistance change arising from the thermal effect in the

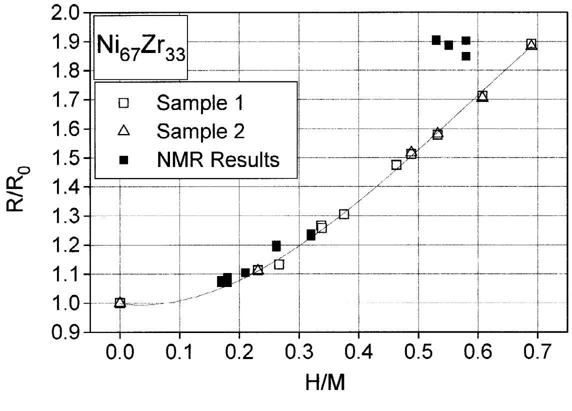

Fig. 3. Normalized resistance versus hydrogen-content measured by weight change or NMR.

as-quenched samples at 393 K, so the reference value R_0 is valid through the whole desorption process.

In Fig. 3. the H/M values obtained by CPMG echo train method are also plotted. A systematic deviation from the results of the weight measurements is visible at higher values of H/M, which is in qualitative agreement with the results of [8] obtained on $Ni_{50-x}Cu_xZr_{50}$ alloys.

3.3. Temperature and pressure dependence of R/R_0

In analogy to pressure–composition isotherms, the equilibrium value of R/R_0 versus ambient pressure are plotted in Fig. 4. for binary $Ni_{67}Zr_{33}$ samples at different temperatures. Samples were charged in the pressure range of 0.1–86 MPa H_2. As it is clearly seen, the equilibrium value of R/R_0, also the H/M, decreases as the temperature rises. This behavior is typical for the hydride-forming alloys showing a negative heat of formation with hydrogen [9].

3.4. The influence of the Cu content (x) on the time of repeated saturations

The characteristic times of the saturation process in binary and ternary glasses are collected in Table 1 for the third charging, using two parallel samples, the same surface treatment, H_2 pressure of 6 MPa at 373 K. It shows, that the charging time and the inhomogeneous character of the saturation grows with Cu-content. The possible interpretation might be that the surface segregation of Cu can hinder either the H-dissociation on the surface or the penetration into the bulk sample.

Table 1
Characteristic time intervals for the repeated chargings of 2–2 parallel $Ni_{67-x}Cu_xZr_{33}$ samples

x	t_{30-90} [min]		t_{50-99} [min]	
	Sample 1	Sample 2	Sample 1	Sample 2
$x=0$	64.0	–	54.9	–
$x=6$	83.0	65.0	65.3	49.4
$x=16$	319.7	118.2	296.9	90.8
$x=33$	–	–	380.0	170.9

3.5. The volume activation and the H-induced chemical reordering

Several papers describe how the H-absorption may be coupled to a phase separation in several transition metal-based metallic glasses [7,10]. The local chemical order of these segregated (often nanometer-scale) clusters differs from the composition of the as-quenched glass. So the quenched-in short range order, (which is predetermined by the composition and the processing conditions) is modified as the H-atoms are introduced into the metallic host. This ordering takes place mostly during the first saturation, but also proceeds slowly with the increasing number of subsequent cycles [7]. Diffusion of the metal atoms in this ordering is also involved. The rate of diffusion for metallic components is lower by several order of magnitude than that for hydrogen at the same temperature. Therefore, the former process is the rate-determining factor in the H-induced chemical ordering. This way, the chemical ordering would be responsible for the process of the volume-activation and it can also contribute to the observed large difference between the time-scales of the first and subsequent saturations.

At the same time, a fraction of H-atoms are trapped into the chemically modified tetrahedral sites. The strongly bound H-atoms are practically immobile at the temperature of cycling, as it is supported by the analysis of the NMR results of the H-saturated amorphous alloys [11]. These immobile H-atoms are responsible for the fact that $R/R_0=1$ cannot be reproduced on the desorption side of the cycling at the temperature of charging.

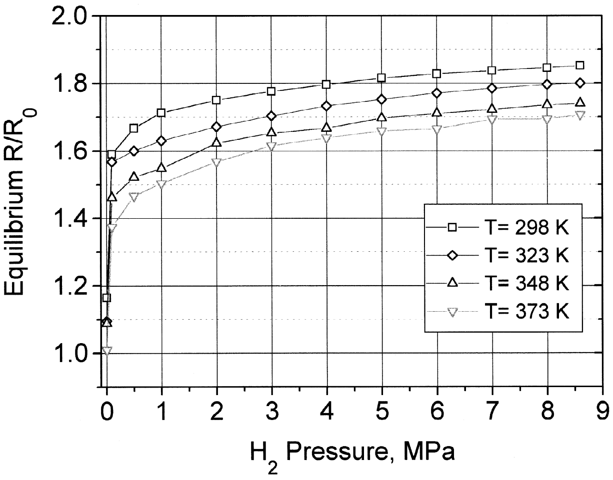

Fig. 4. The characteristics of R/R_0 at different temperatures and ambient H_2 pressures.

4. Summary

Charging and discharging processes were studied by in-situ resistance measurements in $Ni_{67-x}Cu_xZr_{33}$ glassy alloys.

The normalized resistance (R/R_0) is correlated with the hydrogen content. The saturation values of R/R_0, are determined as a function of pressure at different temperatures. The time of saturation is increased by the addition of Cu into the binary system. The H-induced chemical ordering is considered as the main factor in the determination of the volume activation of H-absorption.

Acknowledgments

The work was supported by the Hungarian Academy of Sciences and by the National Science Foundation under

Grant OTKA-T016670. One of the authors (J.G.) thanks the Soros Foundation for the support of the participation at the MH96 conference.

References

[1] R. Zehlinger, P. Oelhafen and H.J. Güntherodt, *Mater. Sci. Eng., 99* (1989) 253.

[2] G. Petö, I. Bakonyi, K. Tompa and L. Guczi, *Phys. Rev. B, 52* (1995) 7151.

[3] D. Menzel, A. Niklas and U. Köster, *Mater. Sci and Eng. A, 133* (1991) 312.

[4] Y. Yamada and K. Tanaka, *Trans. Jap. Inst. Met., 27* 6 409.

[5] J. Toth, J. Garaguly, K. Tompa, A. Lovas and L.K. Varga, *J. Hydrogen Energy*, accepted for publication.

[6] E. Batalla, Z. Altounian, D.B. Boothryod, R. Harris and J.O. Strom-Olsen in: G. Bambakidis and R.C. Bowman Jr. (eds.), *Hydrogen in Disordered and Amorphous Solids*, NATO ASI Ser. B: Physics Vol., 136 (1986) 203.

[7] J. Garaguly, A. Lovas, Á. Cziráki, M. Reybold, T. Takács and K. Wetzig. *Proc. 9th Int. Conf. on Rapidly Quenched Metals*, Bratislava (1996) in press.

[8] K. Tompa, P. Bánki, C. Hargitai, G. Lasanda and L.K. Varga, *J. All. Comp., 232* (1996) 84.

[9] J.D. Fast, *Interaction of Metals and Gases* Vol. 1, Cleaver-Hume Press, Philips Technical Library, Netherlands, 1965, p. 207.

[10] I. Nagy, I. Bakonyi, A. Lovas, E. Tóth-Kádár, K. Tompa, A. Cziráki and B. Fogarassy, *J. Less-Common Met., 167* (1991) 283.

[11] K. Tompa, P. Bánki, C. Hargitai, G. Lasanda, A. Lovas, and L.K. Varga, *J. Alloys Comp., 253–254* (1997) 428–431.