The Electrochemical Hydrogen Sorption Behaviour of Zr–Cu–Al–Ni Metallic Glasses

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Amorphous Zr–Cu–Al–Ni alloys are of interest for hydrogenation studies because they consist of a combination of early and late transition metals. Potentiodynamic polarisation tests were conducted to investigate the cathodic hydrogen reduction reactions on the surface of melt-spun $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ and $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ ribbons. In the Tafel region, the electroodic desorption reaction is the rate-determining step which competes with the hydrogen absorption reaction. In the next polarisation region, the hydrogen reduction takes place under mass transfer-control. The ribbons are galvanostatically charged with hydrogen to different hydrogen-to-metal ratios in 0.1 mol/l NaOH solution. The rate of hydrogen absorption of the $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ alloy is higher than that of the $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ alloy, although the hydrogen discharge rate on the surface of the $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ alloy is higher. Upon charging the samples at room temperature to $\text{H/M} = 1.3$ using a low charging rate (-1 mA/cm^2), the X-ray diffraction pattern show the main peaks of a Zr-hydride and Cu and/or a Cu rich phase(s) besides the amorphous phase. The potentiostatic double-pulse technique (PDP) was applied to estimate the fraction of reversibly absorbed hydrogen in the amorphous alloy samples by charging at different cathodic potentials. Subsequently, the residual hydrogen concentration (irreversibly absorbed hydrogen) was determined by hot extraction. The $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ alloy was found to absorb a higher fraction of reversible hydrogen than the $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ alloy.

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1. Introduction

Zr–Cu–Al–Ni metallic glasses are one of the recently developed alloy systems exhibiting a high glass-forming ability, a wide undercooled liquid region and a high thermal stability.^{1–3} Since the alloy composition contains early transition metals (ETM) and late transition metals (LTM), the amorphous phase will consist of a short-range order of mainly distorted tetrahedral structural units which are favourable for hydrogen occupancy. This makes metallic glass alloys of ETM/LTM a good target for hydrogen investigations. Hydrogen has been used as a probe to explore the distribution of interstitial sites in the amorphous phase of these alloys.⁴ Hydrogen investigations done on Zr–Ni metallic glasses using neutron scattering,⁵ followed by a statistical model for the hydrogen absorption of amorphous LTM/ETM alloys⁶ proposed that the lowest energy hydrogen sites are those surrounded by four ETM atoms, so that: $E_4 < E_3 < E_2 < E_1 < E_0$, where E_n is the energy of hydrogen in $\text{A}_{(4-n)}\text{B}_n$ tetrahedral interstitial sites. This means that for glassy Zr–Ni alloys, the tetrahedral interstitial sites which hydrogen may occupy are in the following energy order: $\text{Zr}_4 < \text{Zr}_3\text{Ni} < \text{Zr}_2\text{Ni}_2 < \text{ZrNi}_3 < \text{Ni}_4$. This model was proved to be valid also for ternary glassy alloys such as Zr–Ni–Cu,⁶ and it is possible that these interstitial sites exist in the quaternary alloys, e.g. Zr–Cu–Al–Ni. Further investigations of the effect of hydrogen on equiatomic Zr–Ni⁷ and $\text{Zr}_{50}\text{Ni}_{50-x}\text{Cu}_x$ ⁸ alloys revealed that the hydriding process induces phase separation by the formation of regions enriched in Ni and/or Cu. The thermal behaviour (stability and desorption) of the Zr–Cu–Al–Ni metallic glasses in combination with the crystallisation behaviour in presence and absence of hydrogen was studied in detail.⁹ Besides, the effect of hydrogen in presence of oxygen and hydrogen on the quasicrystalline phase was in-

vestigated.¹⁰ Nevertheless, electrochemical studies of hydrogen mechanism in metallic glasses^{11,12} are still very limited compared to the considerable progress that has been made in crystalline metals and alloys.^{13–15}

The cathodic hydrogen absorption reaction (HAR) of a metallic material in an aqueous solution is a multi-step process and competes with the hydrogen evolution reaction (HER).¹⁶ Different kinetic paths and mechanisms of the cathodic hydrogen reduction reactions were derived from the Butler-Volmer equation depending on the value of the transfer coefficient,¹⁷ so that by estimating the Tafel slope of the cathodic polarisation curve, it is possible to predict the mechanism of the hydrogen reduction on the surface.

In this paper, the mechanism of the cathodic hydrogen reactions on the surface of amorphous Zr–Cu–Al–Ni alloys were investigated as an initial step for hydrogenation. The effect of hydrogen absorption at room temperature on the amorphous phase was studied. In addition, a determination of the reversibly and irreversibly absorbed hydrogen was performed.

2. Experimental

2.1 Sample preparation and characterisation

The starting ingots of the alloy compositions $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ and $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ were prepared by arc melting Zr, Al, Cu and Ni with a purity of 99.9% in an argon atmosphere. For achieving a high homogeneity, the samples were remelted several times. From the master alloy, ribbons with a thickness of 40 μm and a width of 4 mm were prepared in a single-roller Bühler melt spinner under argon atmosphere. Immediately before hydrogen charging and before applying the electrochemical investigations, the surface of the samples was ground with emery paper of 600-grade and then cleaned ultrasonically with acetone.

X-ray diffraction (XRD) with Co $\text{K}\alpha$ radiation was used to

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investigate the microstructure of the as-prepared and hydrogenated samples. In addition, selected samples were characterised by transmission electron microscopy (TEM) including energy-dispersive X-ray (EDX) analysis.

2.2 Hydrogenation and electrochemical methods

Hydrogenation was performed galvanostatically in 0.1 mol/l NaOH electrolyte containing 5×10^{-5} mol/l As_2O_3 as a hydrogen entry promoter. The current densities applied to investigate the rate of hydrogen absorption were -1 , -10 , -20 and -40 mA/cm² for different time intervals. The hydrogen content was measured by hot extraction using a LECO 402 hydrogen analyser.

The polarisation studies were carried out by means of a conventional 3-electrode cell, using saturated calomel electrode (SCE) as a reference electrode and a Pt foil as a counter electrode, in a deaerated 0.1 mol/l NaOH + 5×10^{-5} mol/l As_2O_3 solution. Potentiodynamic current density-potential curves were recorded using a potential scan rate of 2 mV/s and are shown in terms of a semi-logarithmic Tafel plot. In order to study the mass transfer effect, selected experiments were performed using a rotating disc electrode using rotation speeds of 1000 and 2000 rpm.

In addition, potentiostatic double pulse measurements (PDP) were conducted. The principle of the PDP technique is explained in detail in.¹⁴⁾ Samples were charged with hydrogen at a constant cathodic hydrogen charging potential (E_c) for a time (t_c), so that hydrogen was allowed to enter the sample. The potential was then immediately stepped in the positive direction to a value, E_0 7 mV more negative than the open-circuit potential to avoid measuring anodic currents for any other contributions e.g. oxide layer formation. Due to this potential step, some of the absorbed hydrogen atoms diffuse back from the bulk of the sample to the entry surface and get oxidised. Thus, the measured anodic current transient (i_d) is due to the oxidation of the hydrogen atoms on the entry surface. From the transients the anodic charge (q_a) was. The E_c values were selected at -1 , -1.2 and -1.5 V and t_c for 1 minute so that only small hydrogen concentrations were allowed to enter the samples. Anodic transients were measured for 5 min. Several successive charging/discharging pulses were applied and after the PDP test, the residual hydrogen was measured by hot extraction using a LECO 402 hydrogen analyser.

3. Results and Discussion

3.1 Hydrogen reduction on Zr–Cu–Al–Ni metallic glass surfaces

The cathodic polarisation curves are displayed in Fig. 1 for freshly polished $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ and $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ alloy samples recorded at a potential scan rate of 2 mV/s in deaerated 0.1 mol/l NaOH electrolyte containing 5×10^{-5} mol/l As_2O_3 . In the cathodic region of the semi-logarithmic current density-potential plot, the Tafel plot corresponds mainly to the hydrogen reduction reaction on the sample surface without any considerable other contributions of side reactions such as oxide layer formation.

The cathodic Tafel plot potential range exhibits an increase of the cathodic current density (i_c) immediately after the

Fig. 1 Cathodic Tafel plots of the as-quenched amorphous $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ and $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ alloys recorded in deaerated 0.1 mol/l NaOH + 5×10^{-5} mol/l As_2O_3 solution using a scan rate of 2 mV/s.

Table 1 Kinetic derivatives of mechanisms of hydrogen reduction reactions.¹⁷⁾

Mechanisms	Transfer coefficient, α	Tafel slope, b_c
Rate-determining hydrogen discharge followed by fast chemical desorption	0.5	$2RT/F \equiv 0.44$ V
Fast hydrogen discharge followed by rate determining chemical desorption	2	$RT/2F \equiv 0.11$ V
Fast hydrogen discharge followed by rate-determining electrodic desorption	1.5	$2RT/3F \equiv 0.147$ V

mixed potential (E'). This is named as *Tafel region* and is followed by a *plateau region* which is characterised by an insignificant increase of i_c over a wide range of potentials. At more negative potentials, i.e. in the *high polarisation region*, i_c increases once again. Both alloy compositions exhibit similar cathodic current density-potential behaviour indicating that, the overall hydrogen reduction process is the same.

In the *Tafel region*, the mechanism of the hydrogen reduction reactions can be derived from the cathodic Tafel slope (b_c). From Fig. 1 the estimated cathodic Tafel slope is equal to 0.14 V/dec for both alloys.

A relation between the current density of the hydrogen discharge close to the equilibrium and the overpotential (η) is given by the Butler-Volmer equation:¹⁷⁾

$$i_c = 2FkC(1 - \theta) \exp(-\beta F\eta/RT)$$

where θ is the surface coverage by adsorbed hydrogen atoms, β is a symmetry factor, k is the reaction rate, F is Faraday's constant, and C is the H_3O^+ concentration at the alloy-solution interface. By assuming that the symmetry factor β is equal to the transfer coefficient (α) and by solving this equation for various rate conditions of the reaction paths, the mechanism of the hydrogen reduction can be derived for different Tafel slopes. These data are tabulated in Table 1.

Comparing the Tafel slopes in Table 1 and the Tafel slope calculated from the polarisation curves of the Zr-based alloys in Fig. 1, one may propose that the mechanism of hydrogen

reduction reactions in the Tafel region is a fast hydrogen discharge reaction on the sample surface, followed by a rate-determining electrodic desorption reaction.

Bockris and Tacker¹⁸⁾ proposed a model for the hydrogen entry into the metal. In this model, the hydrogen absorption reaction and the hydrogen recombination reactions (chemical and electrodic desorption) are always competing, and the absorption reaction is a fast step meaning that equilibrium is at-

Investigations using a rotating disc electrode were carried out in order to study the effect of mass transfer in the plateau region of the polarisation curve shown in Fig. 2 for a $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ sample. It is obvious that the plateau region is significantly affected by rotation in a way that the plateau current density increases with increasing rotation speed. This indicates that the mechanism in this potential region is proton diffusion-controlled. A similar effect was observed for the $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ alloy.

In the high polarisation region (Fig. 1), i_c further increases. At such high negative potentials the hydrogen reduction reactions [reactions 1 and 2] besides the hydrogen absorption reaction [reaction 3] are taking place intensively.

Comparing the polarisation curves of the glassy $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ and $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ alloys in Fig. 1, the cathodic current density i_c and the exchange current density (i_0) of $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ alloy are higher than those of $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$, but the difference in the mixed potential E' between the two different alloys is negligible. The polarisation parameters are given in Table 2. These results indicate that the hydrogen discharge as well as the hydrogen evolution

tained rapidly and the absorption reaction proceeds with little activation energy.

In summary, the mechanism of hydrogen reactions in the Tafel potential region for Zr–Cu–Al–Ni metallic glasses in alkaline media can be described by the following equations, where H_{ads} is a hydrogen adsorbed atom and H_{abs} is a hydrogen absorbed atom:

reactions are higher on the surface of the $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ alloy.

3.2 Hydrogen absorption characteristics at room temperature

In Fig. 3 the rates of hydrogen absorption of the $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ and $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ ribbons are shown for different charging current densities. The amorphous $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ alloy absorbs more hydrogen than the $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ alloy, i.e. up to a maximum H/M = 1.65 for $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ alloy as compared to 1.5 for $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ alloy. Yet, in the first 30 hours, the hy-

Table 2 The polarisation parameters of the $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ and $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ alloys in deaerated 0.1 mol/l NaOH + 5×10^{-5} mol/l As_2O_3 solution using a scan rate of 2 mV/s.

Polarisation parameters	$\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$	$\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$
Mixed potential, E'/V (SCE)	−0.468	−0.454
Exchange current density, $i_0/\mu\text{A}/\text{cm}^2$	24	36

Fig. 2 Cathodic Tafel plots of $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ alloy samples measured in deaerated 0.1 mol/l NaOH + 5×10^{-5} mol/l As_2O_3 solution using a scan rate of 2 mV/s; (a) under stagnant conditions; (b) sample rotation at 1000 rpm; (c) sample rotation at 2000 rpm.

Fig. 3 Hydrogen absorption rate of $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ (dashed-lines) and $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ (solid-lines) metallic glass samples using different charging current densities (−1, −10, −20 and −40 mA/cm²) at room temperature.

Fig. 4 XRD patterns of the as-quenched and hydrogenated $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ metallic glass samples ($H/M = 1.3$) at room temperature using different charging conditions.

hydrogen absorption rate of the $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ samples is lower than that of the $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ samples for all charging current densities. This may be due to the high hydrogen evolution reaction on the surface of the $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ alloy as it is indicated from the polarisation curves.

It is assumed that the stoichiometric difference is responsible for the observed lower hydrogen absorption rate and the higher hydrogen evolution rate of the $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ alloy. Since $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ contains more Zr and Ni than $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$, more hydrogen atoms are discharged and adsorbed on its surface. This may increase the probability of recombination and desorption of the adsorbed hydrogen atoms on the surface of the $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ alloy.

The XRD patterns of the $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ alloy samples are illustrated in Fig. 4. For an as-quenched ribbon and for a ribbon charged up to $H/M = 1.3$ using a fast charging rate corresponding to a current density of -20 mA/cm^2 for 60 hours, the XRD patterns show that the amorphous structure seems to be retained. However, for the charged samples the characteristic broad maxima of the amorphous state shift to lower scattering angles in comparison to the uncharged alloy, indicating an expansion of the amorphous structure by hydrogen absorption. This becomes more pronounced with increasing hydrogen concentration. On the other hand, the pattern of a ribbon hydrogen-charged $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ to the same H/M ratio at low charging conditions -1 mA/cm^2 (see Fig. 4) for 600 h reveals the main peaks of Zr-hydride and Cu and/or Cu-rich phase(s) such as cubic Cu_4Al . This result is confirmed by EDX analysis upon TEM investigations of a charged sample which detected the enrichment of Cu and/or Cu-rich phases in the amorphous matrix, as well as an Al enriched area.¹⁰⁾

One can conclude from these results that at room temperature and at very high hydrogen contents, rearrangement of

Fig. 5 Relation between the anodic charge (q_a) and the number of successive charging/discharging pulses using different charging potentials, $E_c = -1$, -1.2 and -1.5 V for one minute.

the amorphous matrix takes place in a way that hydrogen induces Cu clustering, Al enrichment on the alloy surface, and Zr-hydride formation is possible. This change in the amorphous matrix can be attributed to absorbed hydrogen atoms which tend to increase the number of sites of high affinity to hydrogen in the bulk of the alloy *i.e.* the number of Zr sites.

3.3 Reversibility of the absorbed hydrogen

The reversibility of the absorbed hydrogen atoms was studied by means of the potentiostatic double pulse technique. Before discussing the results, it should be emphasised that during *short* charging pulses of one minute, and *low* applied cathodic potential, *e.g.* -1 V , the existing interstitial sites of low and high energy are partially occupied with hydrogen atoms.

Figure 5 shows the calculated anodic charge q_a determined from 10 successive charging/discharging pulses for $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$. As expected, q_a increases by increasing the applied cathodic potential E_c , indicating that more reversibly absorbed hydrogen atoms are absorbed and, consequently, desorbed during discharging. For all charging potentials, q_a increases at the beginning before it attains almost constant values at higher pulse numbers. It is assumed that by applying successive pulses the thin oxide layer which is readily formed on the sample surface is reduced. After that, the amount of the reversibly absorbed hydrogen that can be attained from the charge/discharge pulses is almost constant.

The residual hydrogen content was determined after applying 15 charging/discharging pulses for the different charging potentials in order to detect the irreversibly absorbed hydrogen. In addition, hydrogen was analysed in the as-prepared sample as a "reference" value and the data are given in Table 3. In this table, there is no increase in the residual hydrogen content after charging at $E_c = -1 \text{ V}$ compared to the as-prepared sample. This indicates that there are no detected irreversibly absorbed hydrogen atoms under these detection limit. A similar observation was made for the $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ alloy. At $E_c = -1.2$ and -1.5 V , the residual amount of hydrogen increases in addition to the increase of the amount of the reversible hydrogen as expressed by the increase of q_a in Fig. 5. One may conclude that when

Table 3 The residual hydrogen content (H/M) determined for $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ samples after applying 15 charging/discharging pulses at $t_c = 1$ minute and for the as-prepared sample as a reference.

Charging potential, E_c/V	Residual H/M values
reference	0.0025
–1	0.0017
–1.2	0.004
–1.5	0.008

Fig. 6 Relation between the anodic charge q_a and the number of successive charging/discharging pulses for the $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ and $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ metallic glass samples using a charging conditions of -1 V for one minute.

the amount of hydrogen atoms absorbed at the charging pulse increases, the probability of occupying irreversible sites increases, that's beside the reversible sites.

A comparison between the q_a values of the $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ and $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ alloys using a charging potential -1 V for one minute are revealed in Fig. 6. It is obvious that q_a of the $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ alloy is higher than that of the $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ alloy for all pulses. This can be discussed with respect to the results shown in Fig. 3. For short charging times, the $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ alloy absorbs less hydrogen than the $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ alloy and, consequently, desorbs a lower amount of reversible hydrogen during the discharge pulse, because the hydrogen evolution reaction on the surface of $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ alloy is more pronounced.

4. Summary

(1) The cathodic polarisation curves of Zr–Cu–Al–Ni metallic glasses reveal three characteristic potential regions. In the Tafel region, the mechanism of the hydrogen reduction reactions is a fast hydrogen discharge reaction step followed by a rate-determining electroodic desorption step and the hydrogen absorption reaction is a fast competing step to the electroodic desorption. In the second potential region, the cathodic current density exhibits a plateau and the mechanism is under hydrogen mass transfer control. In the third cathodic potential region, the cathodic current density increases, and

the hydrogen reduction reactions are taking place intensively.

(2) The $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ alloy shows a higher surface activity for the hydrogen discharge reaction as well as for the hydrogen evolution reaction than the $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ alloy. This is attributed to the higher fraction of the Zr and Ni contents which increases the surface coverage with adsorbed hydrogen atoms. Hence, the probability of recombination of the adsorbed atoms on the surface increases. It is assumed that this lowers the hydrogen absorption rate of the $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ alloy.

(3) Absorption of high hydrogen concentrations by the Zr–Cu–Al–Ni metallic glasses under slow electrolytic charging conditions at room temperature yields Cu-clustering at the surface combined with Zr-hydride formation. It is assumed that the absorbed hydrogen induces rearrangement of the amorphous matrix in a way that it increases the number of Zr sites of high affinity to it in the bulk of the alloy.

(4) The amount of reversibly absorbed hydrogen in the $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ alloy is less than that of the $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ alloy. This is assumed to be due to the higher rate of the hydrogen evolution reaction on the surface of the $\text{Zr}_{65}\text{Cu}_{17.5}\text{Al}_{7.5}\text{Ni}_{10}$ alloy which results in the absorption of less amounts of hydrogen during the charging pulse.

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