Site Energy Distributions of Hydrogen Atoms in Ni-Zr Alloy Glasses Studied by Thermal Desorption Spectrometry

By Takeshi Araki*, Tetsurou Abe* and Kazuhide Tanaka*

Thermal desorption spectra (TDS) of hydrogen from Ni-Zr alloy glasses are studied experimentally and theoretically. The spectra manifest composite peaks which change systematically with the hydrogen content and alloy composition. Defining a site energy distribution function, $N(E)$, for the dissolved hydrogen atoms and employing a surface recombination model for the desorption kinetics, TDS spectra are calculated and compared with the experiment. The simulated $N(E)$ function has a few Gaussian peaks, and they are attributed to the hydrogen occupancy in quasitetrahedral interstices with different site energies in these glasses.

(Received June 2, 1989)

Keywords: hydrogen, desorption, Ni-Zr alloy glasses, site energy distribution, surface recombination model, simulation, tetrahedral hole

I. Introduction

The structure and properties of hydrogen-charged amorphous alloys have attracted growing scientific and technological interests in recent years⁽¹⁾⁽²⁾. One of the fundamental concerns in these studies is to reveal what kinds of interstitial sites are really occupied by hydrogen atoms. X-ray and neutron diffraction studies have shown that hydrogen atoms in early transition metal-late transition metal alloy glasses, such as Pd-Zr⁽³⁾, Ni-Zr⁽⁴⁾, Ni-Ti⁽⁵⁾, Cu-Ti⁽⁶⁾ and Fe-Ti⁽⁷⁾ alloys, enter quasitetrahedral sites whose geometrical and chemical atomic configurations usually differ from those in the corresponding crystalline compounds. As a consequence of random atomic arrangements, the potential energy of a hydrogen atom in an alloy glass differs from site to site even for one kind of interstices with a similar chemical environment. These structural features of alloy glasses lead one to define a site energy distribution function, $N(E)$, to describe the thermodynamic behavior of hydrogen atoms in the glasses⁽⁸⁾⁻⁽¹³⁾. Data on the solid solubility⁽⁸⁾⁽⁹⁾, pressure-composition

isotherm⁽¹⁰⁾, long-range diffusion⁽¹¹⁾⁻⁽¹³⁾ and internal friction⁽¹⁴⁾⁻⁽¹⁶⁾ have been successfully analysed using this statistical formula.

In our previous study⁽¹⁷⁾⁽¹⁸⁾, we have shown that the thermal desorption spectrometry (TDS) is a promising technique to obtain $N(E)$ experimentally. In this technique, a sample is continuously heated in dynamic vacuum, and the desorption rate of H₂ gas out of the sample is measured by monitoring its partial pressure against temperature. A TDS model has been developed for alloy glasses in which hydrogen atoms residing on surface sites of a sample are released to the vacuum via a recombination reaction at the surface. The fraction of the surface sites trapping hydrogen atoms is determined by applying the Fermi-Dirac statistics to the dissolved hydrogen atoms where the chemical potential μ_H is implicitly determined by $N(E)$ and the hydrogen content $x=[H]/[M]$. Approximating $N(E)$ by a set of a few Gaussians, TDS spectra are calculated and compared with the observed ones. The Gaussian parameters are adjusted so that a good fit is obtained between the calculation and the experiment. Sputter-deposited Fe-Ti amorphous films and melt-spun Ni-Zr glassy ribbons charged with hydrogen have been studied by this technique.

The purpose of the present work is to examine in more detail the composition depen-

* Department of Materials Science and Engineering, Nagoya Institute of Technology, Showa-ku, Nagoya 466, Japan.

dence of the TDS spectra for Ni-Zr alloy glasses using $\text{Ni}_{64}\text{Zr}_{36}$, $\text{Ni}_{50}\text{Zr}_{50}$ and $\text{Ni}_{33}\text{Zr}_{67}$ alloys, and to discuss the physical meaning of the underlying $N(E)$ functions for these samples derived by the simulation.

II. Experimental Procedure

The principle and procedure of the thermal desorption spectrometry were described in detail in a previous paper⁽¹⁸⁾. The spectra were measured with a vacuum extraction gas analysing system equipped with a quadrupole mass spectrometer and a turbo-molecular pumping unit. The partial pressure of the released H_2 gas in the analysing chamber in the range 10^{-6} to 10^{-3} Pa, when a sample was heated at a constant rate of $(1/6)$ K/s, was continuously recorded with a microcomputer and converted to the desorption rate $-dx/dt$. The partial pressures of other gas species such as O_2 , N_2 , CO_2 and H_2O were also measured simultaneously, but their fractions were negligibly small. Glassy Ni-Zr alloy ribbons produced by melt spinning were charged with hydrogen through reaction with H_2 gas of 1 to 2 MPa at 473 K. The electrical resistances of some of the specimens were measured during gas charging and subsequent thermal releasing, and were compared with the TDS results.

III. Results

Figure 1 shows TDS spectra (lower part) of $\text{Ni}_{64}\text{Zr}_{36}$ glass ribbons with initial hydrogen concentrations up to $x=0.57$. The crystallizing temperature T_x of this glass determined by the electrical resistance measurement was 830 K, well above the TDS peak temperatures. Thus the dissolved hydrogen is entirely desorbed out of the specimens before the crystallization takes place. A small desorption peak observable at ~ 700 K for $x=0.01$ shows up and shifts toward lower temperatures with increasing x with a small hump left around 550 K. The arrows in the figure indicate characteristic positions where main peaks or humps are present in the spectra. It is noteworthy that the higher temperature portion of each spectrum precisely coincides with one another. This is an im-

Fig. 1 TDS spectra for $\text{Ni}_{64}\text{Zr}_{36}$ alloy glass with initial hydrogen contents x shown in the figure (lower part), and the variation of x with temperature obtained by integrating the TDS spectra (upper part). The arrows show characteristic positions of peaks or humps of the spectra.

portant feature of the TDS spectra for modeling the desorption kinetics in glassy alloys. The variation of x with temperature (upper part) is obtained by integrating each desorption peak.

Figure 2 shows TDS spectra for $\text{Ni}_{50}\text{Zr}_{50}$ alloy glass with $x=0.23$ to 0.86 ⁽¹⁸⁾. Since the crystallizing temperature T_x for this glass is 740 K, a certain fraction of the dissolved hydrogen is released after it is crystallized to a NiZr compound⁽¹⁹⁾, as revealed by sharp peaks above the T_x . A main peak accompanying a higher-temperature hump is seen in a heavily charged specimen, whose peak temperature is definitely higher than that of the $\text{Ni}_{64}\text{Zr}_{36}$ glass of a similar hydrogen content.

Figure 3 shows TDS spectra for $\text{Ni}_{33}\text{Zr}_{67}$ alloy glass with $x=0.93$ to 1.40 . The crystallization occurs at 680 K in this glass, so that most of the hydrogen is desorbed above T_x , where the glass is transformed to a mixture of crystalline NiZr hydride and ZrH_2 ⁽¹⁹⁾. The desorption peak from the glass phase is small

Fig. 2 TDS spectra for $\text{Ni}_{50}\text{Zr}_{50}$ alloy glass with initial hydrogen contents shown in the figure, and the variation of x with temperature.

Fig. 3 TDS spectra for $\text{Ni}_{33}\text{Zr}_{67}$ alloy glass with initial hydrogen contents shown in the figure, and the variation of x with temperature.

Fig. 4 Relationship between the normalized electrical resistance R/R_0 at 300 K and hydrogen content x for $\text{Ni}_{50}\text{Zr}_{50}$ glass ribbons. The inset shows the variation of R/R_0 with charging time under H_2 gas atmosphere of 2 MPa at 448 K.

Fig. 5 Variation of R/R_0 of H-charged $\text{Ni}_{50}\text{Zr}_{50}$ alloy ribbons ($x=0, 0.4$ and 0.8) with temperature (upper curves), and the corresponding derivative spectra (lower curves).

and is further shifted toward higher temperature in comparison with the alloys of lower Zr concentrations. Practically no desorption peak is observable below T_x in specimens of lower hydrogen contents than $x=1.0$.

Now, the electrical resistance of a hydrogenated $\text{Ni}_{50}\text{Zr}_{50}$ glass ribbon increases almost proportionally to the hydrogen content as shown in Fig. 4, where a relationship between x and the electrical resistance normalized to that before charging, R/R_0 , is displayed. The inset shows how it varies with charging time under H_2 gas of 2 MPa at 448 K. This resistance increment is recovered by hydrogen desorption during subsequent heating, as shown in Fig. 5. One finds that the variations of R/R_0 and its derivative with hydrogen contents are qualitatively similar to those of x and the TDS spectrum shown in Fig. 2, respectively. The discrepancy of the peak temperatures between the two measurements may be due to a smaller heating rate, $\sim (1/60)$ K/s, employed for the electrical resistance measurements, as compared with $(1/6)$ K/s for the TDS measurements.

IV. Discussion

1. The TDS model for glassy alloys

We have shown in our previous paper⁽¹⁸⁾ that the desorption of hydrogen from a glassy alloy is well described by a schematic potential diagram as illustrated in Fig. 6⁽¹⁸⁾. A hydrogen

Fig. 6 Schematic potential energy diagram for a hydrogen atom around a surface site and interior disordered sites in a glassy alloy. The site energy distribution function, $N(E)$, is shown to the left side of the diagram.

atom residing on a surface site of energy g_s recombines with another atom to form a H_2 molecule via a transition state g^* . The site energy distribution of H atoms in the bulk is expressed as

$$N(E) = \sum_{i=1}^n C_i G_i(E; g_i, \sigma_i) \quad (1)$$

where C_i is the hydrogen capacity in i th-type sites, G_i is a normalized Gaussian distribution function with the centroid energy g_i and the standard deviation σ_i , and n is the number of the assumed Gaussian functions. Under quasi-chemical equilibrium conditions, the total hydrogen concentration is related to $N(E)$ as

$$x = \int_{-\infty}^{\infty} N(E) f(E) dE, \quad (2)$$

where $f(E)$ is the Fermi-Dirac distribution function given by

$$f(E) = [1 + \exp \{(E - \mu_H)/kT\}]^{-1}. \quad (3)$$

The hydrogen desorption rate is given by the following 2nd-order equation⁽²⁰⁾:

$$-dx/dt = (M_s/M) v_0 \theta_s^2 \exp \{-2(g^* - g_s)/kT\}, \quad (4)$$

where M_s/M is the fraction of surface sites to metal atoms, v_0 the attempt frequency for recombination, and θ_s the hydrogen occupancy at the surface sites given by

$$\theta_s = [1 + \exp \{(g_s - \mu_H)/kT\}]^{-1}. \quad (5)$$

The TDS spectrum can be calculated from equations (1) through (5) when the initial hydrogen concentration is known. To carry out this simulation, we first assume an arbitrary set of Gaussian functions to formulate $N(E)$, calculate $-dx/dt$ versus temperature for a series of initial hydrogen concentrations, and compare them with the observed spectra. If the former are different from the latter, a new set of Gaussians is assumed and subjected to the above calculation. This procedure is repeated until a good fit is obtained between the simulation and the experiment. The following numerical data are used for the calculation: $M_s/M = 10^{-4}$, $g^* - g_s = 58$ kJ/molH. They have been determined by separate TDS

experiments on hydrogen-adsorbed glassy alloys⁽¹⁸⁾.

2. Simulated TDS spectra

Figure 7 shows simulated TDS spectra (lower part) and the underlying $N(E)$ function (upper part) for the $\text{Ni}_{64}\text{Zr}_{36}$ alloy glass. Agreement of the TDS spectra between the simulation and experiment (Fig. 1) appears to be satisfactory. The site energy distribution involves three Gaussians each separated by ~ 15 kJ/molH (the lowest-energy component is very small). Their characteristic parameters, g_i , σ_i and C_i , together with $C_i/C_{\max}$ where $C_{\max} = \sum C_i$ is the net hydrogen capacity, are listed in Table 1. The site energy is scaled with reference to the transition-state energy g^* . To examine the effect of Gaussian broadening of the site energy upon the simulated TDS spectra, the σ_i 's are reduced from ~ 8 kJ/molH of the above simulation to 1 kJ/molH leaving the

Table 1 Numerical parameters for the site energy distribution function, $N(E)$.

Samples	i	g_i (kJ/molH)	σ_i (kJ/molH)	C_i	$C_i/C_{\max}$	$P_{\text{stat}}(j)$
a- $\text{Ni}_{64}\text{Zr}_{36}$	1	-59	7.5	0.40	0.733	0.730(2)
	2	-75	7.5	0.14	0.256	0.240(3)
	3	-96	10	0.01	0.011	0.030(4)
a- $\text{Ni}_{50}\text{Zr}_{50}$	1	-69	4	0.43	0.430	0.545(2)
	2	-82	4.5	0.28	0.280	0.364(3)
	3	-104	5	0.20	0.200	0.091(4)
a- $\text{Ni}_{33}\text{Zr}_{67}$	1	-72	5	0.38	0.271	0.329(2)
	2	-96	1	0.57	0.407	0.445(3)
	3	-106	1	0.45	0.320	0.226(4)

other parameters unchanged. The result is shown in Fig. 8. This reduction of the widths makes the calculated TDS spectra much sharper than those of Fig. 7, as expected, revealing a clear shoulder around 550 K. This spectral feature is, however, inconsistent with

Fig. 7 Site energy distribution function, $N(E)$, and the corresponding TDS spectra for $\text{Ni}_{64}\text{Zr}_{36}$ alloy glass obtained by the simulation. The energy is scaled with reference to the transition state g^* of Fig. 6.

Fig. 8 Simulated TDS spectra for $\text{Ni}_{64}\text{Zr}_{36}$ alloy glass, where the $N(E)$ function is modified in such a way that the widths σ_i 's are all reduced to 1 kJ/molH while the other parameters are retained the same as in Fig. 7.

Fig. 9 Site energy distribution function, $N(E)$, and the corresponding TDS spectra for $\text{Ni}_{50}\text{Zr}_{50}$ alloy glass obtained by the simulation. Effects of crystallization upon the TDS spectra are not taken into account in this simulation.

the observed ones.

Figure 9 shows a similar result for the $\text{Ni}_{50}\text{Zr}_{50}$ alloy glass⁽¹⁸⁾. The site energies for the three Gaussian components of $N(E)$ are shifted by -8 kJ/molH toward the lower energy in comparison with those for the $\text{Ni}_{64}\text{Zr}_{36}$ glass, of which the lowest-energy component is seen to be much enhanced. Their numerical data are listed in Table 1. The simulated TDS spectra well reproduce the features of the observed ones (Fig. 2), except for the sharp components present above T_x ; the effect of the crystallization has not been taken into account in this simulation.

Figure 10 shows a result of simulation for $\text{Ni}_{33}\text{Zr}_{67}$ alloy glass. Since most of the dissolved hydrogen is desorbed above T_x in this glass, two narrow Gaussian peaks ($\sigma_i=1$ kJ/molH) assuming the site energies in crystalline NiZr hydride and ZrH_2 are involved beforehand in

Fig. 10 Site energy distribution function, $N(E)$, and the corresponding TDS spectra for $\text{Ni}_{33}\text{Zr}_{67}$ alloy glass obtained by the simulation. Effects of crystallization upon the TDS spectra have been taken into account by predifining two low-energy Gaussian peaks with $\sigma_i=1$ kJ/molH in the $N(E)$ function.

$N(E)$ for the TDS simulation; the uppermost broad peak assumes the site distribution in the glass phase. Their numerical data are given in Table 1. Though the overall feature of the simulated spectra resembles that of the experiment (Fig. 3), quantitative agreement of these spectra in the glass-state region is not quite satisfactory.

3. Significance of the site energy distribution function

The above comparison of the experimental and theoretical TDS spectra for glassy $\text{Ni}_{1-y}\text{Zr}_y$ alloys shows that $N(E)$ should be composed of at least three Gaussians whose centroid energies and weights depend on the alloy composition; the weights of the lower-energy components increase with increasing Zr concentration. A similar trend has been found

for amorphous $\text{Fe}_{1-y}\text{Ti}_y$ alloys ($y=0.35$ and 0.70)⁽¹⁸⁾. We assume that the site energy of a hydrogen atom is grossly determined by the number of Zr atoms surrounding it. Then, for quasi-tetrahedral interstices, the energy should be increased in the order Zr_4 , Ni_1Zr_3 , Ni_2Zr_2 , Ni_3Zr_1 and Ni_4 holes. The probability of finding the tetrahedral holes with j Zr-atoms is given by⁽⁴⁾

$$f_j = {}_4C_j(1-y)^{4-j}y^j \quad (6)$$

for a random distribution of the constituent atoms. Taking only the holes with $j=2, 3$ and 4 as the possible occupation sites of hydrogen, the statistical fraction of each hole defined by

$$P_{\text{stat}}(j) = f_j / (f_2 + f_3 + f_4) \quad (7)$$

is calculated and put in Table 1 in the decreasing order of the site energy; i.e. $j=2, 3$ and 4 correspond to $i=1, 2$ and 3 , respectively. It is interesting to note that, in the $\text{Ni}_{64}\text{Zr}_{36}$ and $\text{Ni}_{50}\text{Zr}_{50}$ glasses, $P_{\text{stat}}(j)$ has comparable magnitudes with C_i/C_{max} derived by the simulation. Such a comparison is however insignificant for the $\text{Ni}_{33}\text{Zr}_{67}$ glass in which C_i/C_{max} is strongly modified by the crystallization. The above similarity between C_i/C_{max} and $P_{\text{stat}}(j)$ suggests that the presence of the three Gaussian components in $N(E)$ derived by the simulation is a direct consequence of the hydrogen occupancy in quasi-tetrahedral holes environed by two, three and four Zr atoms in these glassy alloys.

Recently, TDS spectra of hydrogen from Pd-Si⁽²¹⁾ and Fe-Ni-Mo-B⁽²²⁾ alloy glasses were measured and discussed in terms of a single-Gaussian site energy distribution. However, the hydrogen capacities in these glasses are limited to very small levels, so that no detailed analysis of the distribution function was possible for these glasses.

V. Summary and Conclusions

Thermal desorption spectra of H-charged Ni-Zr alloy glasses have been measured. The spectra manifest composite peaks whose intensities change systematically with the hydrogen content and alloy composition: the lower-temperature peaks show up with increasing

hydrogen content for a fixed Ni concentration, while they show up with increasing Ni concentration for a fixed hydrogen content. A similar trend of the hydrogen desorption properties has been revealed by electrical resistance measurements. This feature of the TDS spectra can be understood if one assumes that the dissolved hydrogen atoms enter the holes of a few kinds of atomic polyhedra with different site energies, and are evolved upon heating from unstable through stable sites progressively. Expressing a site energy distribution function, $N(E)$, by a set of a few Gaussians and employing a surface recombination model for the desorption kinetics, TDS spectra have been calculated and compared with the experiment. Three Gaussian functions with different weights are necessary to reproduce the observed spectra by the simulation. An examination of the simulated $N(E)$ function suggests that the hydrogen atoms reside on quasi-tetrahedral holes with Zr_4 , Ni_1Zr_3 and Ni_2Zr_2 configurations in the increasing order of site energy in these alloy glasses.

REFERENCES

- (1) K. Suzuki: *J. Less-Common Met.*, **89** (1983), 183.
- (2) A. J. Maeland: *Rapidly Quenched Metals*, Ed. by H. Steeb and H. Warlimont, North-Holland, Amsterdam, (1985), p. 1507.
- (3) K. Samwer and W. L. Johnson: *Phys. Rev.*, **B28** (1983), 2907.
- (4) H. Kaneko, T. Kajitani, M. Hirabayashi, M. Ueno and K. Suzuki: *J. Less-Common Met.*, **89** (1983), 237.
- (5) K. Kai, S. Ikeda, T. Fukunaga, N. Watanabe and K. Suzuki: *Physica*, **B120** (1983), 342.
- (6) B. Rodmacq, Ph. Mangin and A. Chamberod: *J. Phys.*, **F15** (1985), 2259.
- (7) B. Rodmacq, F. Lancon and A. Chamberod: *J. Mater. Sci. Eng.*, **97** (1988), 157.
- (8) R. Kirchheim, F. Sommer and G. Schluckebier: *Acta Metall.*, **30** (1982), 1069.
- (9) R. Kirchheim: *Acta Metall.*, **30** (1982), 1069.
- (10) J. H. Harris, W. A. Curtin and M. A. Tenhover: *Phys. Rev.*, **B36** (1987), 5784.
- (11) R. Kirchheim and U. Stolz: *J. Non-Cryst. Sol.*, **70** (1985), 323.
- (12) R. Kirchheim and U. Stolz: *Acta Metall.*, **35** (1987), 281.
- (13) J. J. Kim and D. A. Stevenson: *J. Non-Cryst. Sol.*, **101** (1988), 187.
- (14) U. Stolz, M. Weller and R. Kirchheim: *Scripta Metall.*, **20** (1986), 1361.
- (15) B. S. Berry and W. C. Pritchett: *Hydrogen in Disordered and Amorphous Solids*, Ed. by G. Bambakidis

- and R. C. Bowman, Jr., Plenum Press, (1986), p. 215.
- (16) B. S. Berry and W. C. Pritchett: J. Mater. Sci. Eng., **97** (1988), 419.
- (17) T. Abe, M. Yamada, O. Yoshinari, K. Tanaka, H. Yasuda, K. Sumiyama and Y. Nakamura: *Proc. of Int'l. Symp. on Non-Equilibrium Solid Phases of Metals and Alloys*, Supplement to Trans. JIM, **29** (1988), p. 435.
- (18) T. Abe, T. Araki and K. Tanaka; J. Japan Inst. Metals, **53** (1989), 635.
- (19) Y. Yamada and K. Tanaka: Trans. JIM, **27** (1986), 409.
- (20) A. Stern, A. Resnik and D. Schaltiel: J. Phys., **F14** (1984), 1625.
- (21) S. M. Lee and J. Y. Lee: Acta Metall., **36** (1988), 605.
- (22) J. B. Han, D. W. Kweon and J. Y. Lee: J. Non-Cryst. Sol., **108** (1989), 216.
-