Long-Range Diffusion of Hydrogen in Amorphous Cu₅₀Ti₅₀

H. Mizubayashi, T. Ishii

► To cite this version:

H. Mizubayashi, T. Ishii. Long-Range Diffusion of Hydrogen in Amorphous Cu₅₀Ti₅₀. Journal de Physique IV Proceedings, 1996, 06 (C8), pp.C8-659-C8-662. 10.1051/jp4:19968142 . jpa-00254575

HAL Id: jpa-00254575

<https://hal.science/jpa-00254575>

Submitted on 1 Jan 1996

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Long-Range Diffusion of Hydrogen in Amorphous $\text{Cu}_{50}\text{Ti}_{50}$

H. Mizubayashi and T. Ishii

Institute of Materials Science, University of Tsukuba, Tsukuba 305, Japan

Abstract. The hydrogen Gorsky effects (HGE) measurements were carried out in amorphous $\text{Cu}_{50}\text{Ti}_{50}$ for which the data for the hydrogen Snoek peak (HSP) have been compiled. In the hydrogen concentration, C_{H} , range below 1 at.%, the hydrogen diffusion process changes over from the short circuit mode to the detrapping mode with increasing C_{H} and $(d\lambda)^2$ is much smaller than $(tr\lambda)^2$, where λ is the strain tensor around a hydrogen atom. For $C_{\text{H}} > 1$ at.%, the hydrogen diffusion proceeds by the detrapping mode. The whole hydrogen atoms contribute to the HGE although only hydrogen atoms sitting on the sites with G being nearly equal to μ contribute to the HSP, where G is the site energy and μ the chemical potential of hydrogen atoms. The results are expected as a dispersion in G is much larger than thermal energies and the nearest neighbor blocking for hydrogen occupation is the case. $(d\lambda)^2$ is much larger than $(tr\lambda)^2$, suggesting that one or two of λ_1 , λ_2 and λ_3 is (are) negative for $C_{\text{H}} > 1$ at. %.

1. INTRODUCTION

The anelasticity study of hydrogen (H) in amorphous (a-) alloys has been ignited and stimulated by Berry and Pritchett [e.g., 1-5]. The hydrogen Snoek peak (HSP) reflecting the short range diffusion gives information about the local atomic structures and the hydrogen Gorsky effect (HGE) due to the long range diffusion provides insight into the site connectivity, respectively. The observed features, however, strongly depend on alloy compositions: For the relaxation strength of the HSP, reported are the almost linear increase with the concentration of hydrogen, C_{H} , in a-Pd_xSi_{100-x} ($x=80, 86$ [2-4]), the camel like C_{H} dependence in a-Cu₅₀Ti₅₀ and a-Cu₅₀Zr₅₀ [6,7] and the intermediate behavior in a-Co₃₃Zr₆₇ [8], where the underlying process for the HSP is in dispute. The pre-exponential factor, $D_{\text{G},0}$, of the chemical diffusion coefficient for the long range diffusion (here, for the HGE) also varies strongly depending on alloy compositions (see Fig.2(b) and [3-5, 9-12]). To pursue the systematic understanding of the behaviors of H atoms in a-alloys, we carried out the HGE measurements in a-Cu₅₀Ti₅₀ for which the HSP data have been compiled.

2. EXPERIMENTAL

Amorphous Cu₅₀Ti₅₀ ribbons of 25 μm thick and 1mm wide were prepared by a melt spinning method in an Ar gas atmosphere. After mechanical polishing in water of the surface layer by 5 μm , hydrogen charging was made electrolytically in 0.1N H₂SO₄ at room temperatures. C_{H} in specimens was estimated by a vacuum extraction method. The HGE was measured as elastic after effects in bending strain in the temperature range between 320 and 340 K, where the gage length of a specimen was about 20 mm. $D_{\text{G},0}$ and the activation energy, E_{G} , in the chemical diffusion coefficient were estimated from the Arrhenius plot of the relaxation time for the HGE and the thickness of specimens. Because of the limited measurement temperature range, the experimental errors in E_{G} are as large as about $\pm 10\%$. Examples of the errors in $D_{\text{G},0}$ will be shown in Fig.2(b). The relaxation strength, Δ_{G} , of the HGE was estimated from the observed relaxation strength after taking into account an elapsed time for prestraining. See [9] for details.

3. RESULTS AND DISCUSSION

3.1 The Hydrogen Concentration Range above 1 at. %

Figure 1(a) shows the C_H dependence of Δ_G observed in as-quenched a-Cu₅₀Ti₅₀ specimens, where the solid line 1 is drawn to guide eyes. In the C_H range above 1 at.%, Δ_G increases almost linearly with C_H showing a deviation at higher C_H . For a dilute interstitial solid solution of crystalline materials, Δ_G can be written [13]

$$\Delta_G = (\nu_0 E / 9 k_B T \beta) (\text{tr} \lambda)^2 C_0 \quad (1)$$

where ν_0 is an atomic volume, E the Young's modulus, k_B the Boltzman factor, β the number of interstitial sites per host atom in the lattice, and λ the strain tensor around an interstitial atom, and C_0 the concentration of interstitial atoms. Using $\text{tr} \lambda = 0.11$ for C_H below 20 at.% which is found after the dilatation measurements [14], $\beta = 3.7$ which is reported for the tetrahedral sites in metal-metal a-alloys [15] and the appropriate values for other quantities [16, 17], the dashed line 2 in Fig. 1(a) is calculated assuming Eq.(1) and $C_0 = C_H$. The Δ_G data observed in the C_H range between 1 and 10 at.% show good agreement with the calculated values, suggesting that the whole H atoms contribute to the HGE in the C_H range. The deviation from the linear increase found for $C_H > 10$ at.% will be mentioned later.

Figure 1(b) shows the C_H dependence of Δ_R/Δ_G for $C_H > 1$ at.%, where Δ_R is the relaxation strength of the HSP observed in as-quenched a-Cu₅₀Ti₅₀ specimens; the curve 3 for the total Δ_R and the curve 4 for the Δ_R -1 of the predominant constituent HSP-1 ([6] and also see Fig.2(a)). Δ_R being fairly larger than Δ_G suggests that $(\delta \lambda)^2$ is much larger than $(\text{tr} \lambda)^2$, i.e., one or two of λ_1 , λ_2 and λ_3 should be negative. As a matter of fact, the X-ray and dilatation measurements [14] indicate that one or two of λ_1 , λ_2 and λ_3 is (are) negative. The C_H dependence of Δ_G being different from that of Δ_R is emphasized. The camel like changes in Δ_R suggest that only H atoms sitting on the sites with G being nearly equal to μ can contribute to the HSP, where G is the site energy and μ the chemical potential of H atoms [6-7].

Figures 2(a) and (b) show the C_H dependence of E_G and $D_{G,0}$, respectively. In Fig.2(a), the activation energies E_m ($m=0-5$) reported for the constituent HSP- m are also shown, where the HSP-1 is always predominant and the constituent Δ_R - m for the HSP- m decreases in the order of $m=1$ to 5, and 0 [6]. For $C_H > 1$ at.%, the values of E_G are similar to those of $E_{m=1}$, where both E_G and $E_{m=1}$ decrease with increasing C_H . In Fig.2(b), the solid line 1 is drawn to guide eyes. The arrow 2 denotes the order of $D_{G,0}$ reported in a-Ni₄₀Zr₆₀ [5] and a-Pd_xSi_{100-x} ($x=80, 86$ [2-4], $x=81, 83$ [10]), the dashed line 3 the order of $D_{G,0}$ in crystalline Cu, Ni, Pd, Nb, Ta and V [18] and the arrow 4 the order of $D_{G,0}$ in a-Fe₄₀Ni₄₀P₁₄B₆ [11] and a-Pd_{73.2}X_{8.2}Si₁₈ ($X=\text{Ni, Cu, Ag, Cr, Fe}$ [12]), respectively. The low value of $D_{G,0}$ indicated by the arrow 4 is suggested to reflect the existence of short circuits such as dislocations in crystalline materials [11]. On the other hand, the high value of $D_{G,0}$ indicated by the arrow 2 is surmised to suggest that H atoms sitting on the sites with $G \leq \mu$ can migrate via the sites with higher G and lower migration activation energies, i.e., detrapping motions [2-4, 9]. The present values of $D_{G,0}$ found for $C_H > 1$ at.% are comparable with $D_{G,0}$ indicated by the arrow 2, and tend to decrease with increasing C_H . The former result suggests that the long range diffusion of H atoms in a-Cu₅₀Ti₅₀ proceeds through detrapping motions. The latter is explained as a result of filling of H sites from the bottom.

We discuss the different C_H dependence found for Δ_G and Δ_R at first. As already reported in a-

Figure 1: The C_H dependence of Δ_G (a) and of Δ_R/Δ_G (b) observed in as-quenched a-Cu₅₀Ti₅₀. See text.

$\text{Cu}_{50}\text{Ti}_{50}$ and $\text{a-Cu}_{50}\text{Zr}_{50}$ [6,7], the camel like changes in Δ_R can be expected when a dispersion in G is much larger than thermal energies and H atoms sitting on the sites with $G < \mu$ do not contribute to the HSP because of the nearest neighbor blocking for vacant sites due to nearby H-atoms. In other words, a distribution of the density of active two level systems is narrow and located at around $G \sim \mu$. In contrast to the HSP, all the H atoms can contribute to the HGE because equilibration in the H occupation can be achieved for any sites through detrapping motions of H atoms. On the other hand, the deviatory decrease in Δ_G found for $C_H > 10$ at.% suggests that one part of H atoms hardly contributes to the HGE in the C_H range, because $\text{tr}\lambda$ remains unchanged for C_H below 20 at.% [14]. We surmise that detrapping motions of H atoms from the sites with lower G are practically retarded due to an increase in activation energies of detrapping or geometrical blocking by an increase in number of nearby H atoms. When a dispersion in G is not so large or a restriction for the site blocking is more moderate than for the nearest neighbor blocking, a linear increase in Δ_R can be expected. As a matter of fact, in $\text{a-Pd}_x\text{Si}_{100-x}$ ($x \sim 80$) [2-4], the observed linear increase in Δ_R is suggested to reflect a moderate restriction for site blocking because of a dispersion in G being much larger than thermal energies. For $\text{a-Co}_{33}\text{Zr}_{67}$ [8], we surmise that a restriction for site blocking is intermediate between those mentioned above because of the intermediate C_H dependence of Δ_R reported.

For the HSP, the constituent HSP-m with lower activation energies than $E_{m=1}$ are observed. On the other hand, E_G found in the HGE is similar to $E_{m=1}$. The results suggest that the activation energies for detrapping motions for the HGE are nearly equal to $E_{m=1}$ and that for the HSP, the constituent HSP-m ($m=0$ and 2 to 5) with lower activation energies are not due to the detrapping motion but through migration between neighboring sites (see Fig.7 in [7]). For the constituent HSP-1, the further work is required to clarify whether the HSP-1 proceeds via migration between neighboring sites or the detrapping motion.

3.2 The Hydrogen Concentration Range below 1 at. %

In Fig.1(a), 2(a) and 2(b) characteristic changes in Δ_G , E_G and $D_{G,0}$ can be seen for C_H below 1 at.%; all the quantities show a steep increase followed by an abrupt decrease with increasing C_H , suggesting that the underlying process for the HGE is different from that for C_H above 1 at.%. The low values of E_G and $D_{G,0}$ found for $C_H < 0.2$ at.% are similar to those reported in $\text{a-Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$ [11] and $\text{a-Pd}_{73.2}\text{X}_{8.2}\text{Si}_{18}$ ($X=\text{Ni, Cu, Ag, Cr, Fe}$ [12]) suggesting the existence of short circuits for the long range diffusion. The steep increases in E_G and $D_{G,0}$ with increasing C_H are explained by a change in the diffusion process from the short circuit mode to the detrapping mode. Since no percolation path spanning the sites with $G \sim \mu$ is expected for such a low C_H range, we surmise that some line defects such as dislocations in crystalline materials which have been

Figure 2: The C_H dependence of E_G (a) and of $D_{G,0}$ (b) observed in as-quenched $\text{a-Cu}_{50}\text{Ti}_{50}$. See text.

suggested in [11] serve as the short circuits. The steep increase in $D_{G,0}$ is explained by filling up of the sites in the line defects by H-atoms. An increasing rate of Δ_G with C_H found for C_H below 1 at.% is about 10 times larger than for C_H above 1 at.%, suggesting a larger value of $(tr\lambda)^2$ for C_H below 1 at.%. On the other hand, such a strong increase in the HSP is not observed for C_H below 1 at.% [6], suggesting that for the sites in the C_H range below 1 at.%, $(\delta\lambda)^2$ is much smaller than $(tr\lambda)^2$ and the maximum H content in the sites is about 1 at.%. Since for C_H above 1 at.%, H atoms occupy the tetrahedral sites in the order of Ti_4 , Ti_3Cu_1 and so on in a-Cu₅₀Ti₅₀, we surmise that the sites responsible for C_H below 1 at.% are the Ti_6 -octahedral sites.

4. CONCLUSION

The C_H range below 1 at.%. The H diffusion process in a-Cu₅₀Ti₅₀ turns from the short circuit mode to the detrapping mode with increasing C_H . For the λ tensor around a H atoms, $(\delta\lambda)^2$ is much smaller than $(tr\lambda)^2$ in the C_H range. We surmise that the H sites in the C_H range are the Ti_6 -octahedral sites and some line defects serve as short circuits.

The C_H range above 1 at.%. The H diffusion in a-Cu₅₀Ti₅₀ proceeds by the detrapping mode where H atoms are known to occupy the tetrahedral sites. The whole H atoms contribute to the HGE although only H atoms sitting on the sites with $G \sim \mu$ contribute to the HSP. These results are expected as a dispersion in G is much larger than thermal energies and the nearest neighbor blocking is the case. For the λ tensor around a H atom in the C_H range, one or two of λ_1 , λ_2 and λ_3 is (are) negative.

Acknowledgements

The authors are grateful to Dr. H. Tanimoto (Univ. of Tsukuba) for his invaluable helps on the course of experiments. This work is partly supported by a Grant in Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

References

- [1] Berry B.S., Pritchett W.C. and Tsuei C.C., Phys. Rev. Lett., **41**(1978), 410.
- [2] Berry B.S. and Pritchett W.C., Phys. Rev. B, **24**(1981), 2299.
- [3] Berry B.S. and Pritchett W.C., "Hydrogen in Disordered and Amorphous Solids", G. Bambakidis and R.C. Bowman, Jr. Eds. (Plenum Press, New York, 1985) p.219.
- [4] Berry B.S. and Pritchett W.C., Z. Phys. Chem., **163**(1989), 381.
- [5] Berry B.S. and Pritchett W.C., Mater. Sci. Engng., **97**(1988), 419.
- [6] Mizubayashi H., Agari H. and Okuda S., Phys. Stat. Sol. (a), **122**(1990), 221.
- [7] Mizubayashi H., Naruse T. and Okuda S., Phys. Stat. Sol. (a), **132**(1992), 79.
- [8] Sinning H.-R., Phys. Stat. Sol. (a), **140**(1993), 97.
- [9] Mizubayashi H., Odai S. and Okuda S., Acta Metall. Mater., **42**(1994), 561.
- [10] Lee T.S. and Stevenson D.A., J. Non-Crystall. Solids, **72**(1985), 249.
- [11] Hofmann A. and Kronmüller H., Phys. Stat. Sol. (a), **104**(1978), 619.
- [12] Yoshinari O. and Kirchheim R., J. Less-Common Metals, **172-174**(1991), 890.
- [13] Nowick A.S. and Berry B.S., "Anelastic Relaxation in Crystalline Solids", (Academic Press, New York, 1972) p.302.
- [14] Sibazaki M. and Mizubayashi H., to be published.
- [15] Ninomiya T., "The Structure of Non-Crystalline Materials", P.H. Gaskell, J.M. Parken and E.A. Davis Eds. (Taylor and Francis Ltd., London, 1982) p.558.
- [16] Tanner L.E., Davis L.A., Chen C.-P. and Ray R., Scripta Metall., **10**(1976), 937.
- [17] Grzeta B., Dini K., Cowlam N. and Davies H.A., J. Phys. F: Met. Phys., **15**(1985), 2069.
- [18] Völkl J. and Alefeld G., "Topics in Applied Phys. Vol.28", Hydrogen in Metals I, G. Alefeld and J. Völkl Eds. (Springer-Verlag, Berlin, 1978), p.321.