Grain Boundary Effect on Diffusion of Hydrogen in Pure Aluminum

Minoru Ichimura*, Yasushi Sasajima* and Mamoru Imabayashi*

Hydrogen diffusivity and solubility in pure solid aluminum were measured in a high temperature range from 573 to 923 K, by means of a desorption technique, which was an outgassing study from thermally hydrogen-charged cylindrical samples with various grain sizes. The diffusion coefficient depended linearly upon an inverse of temperature in the Arrhenius plot. There were two characteristics in the plot; one of them was a change of apparent activation energy for diffusion being a fixed diffusivity at about 900 K, while another was a correlation between the increase of activation energy and the decrease of grain size. We proposed a simple model for grain size dependence of the hydrogen diffusivity. The decrease in diffusivity at a lower temperature for the smaller grain size was explained by trapping of hydrogen at nodes of grain boundaries. In a very large grain size, there was a possibility of a fast diffusion along the grain boundary. The increase in solubility usually expected from a trapping process was not found in this study.

(Received June 26, 1991)

Keywords: aluminum, hydrogen, diffusivity, solubility, grain boundary, enhanced diffusion, trapping

I. Introduction

Diffusivity of hydrogen and its isotopes in pure solid aluminum has been investigated so far widely in the literature⁽¹⁾⁻⁽¹⁶⁾. A comparative survey is shown in Fig. 1 for the temperature dependence of diffusivity, and Table 1 for the diffusivity data and experimental conditions. All the data in the high temperature range in Fig. 1 were measured by the desorption technique in which outgassing from hydrogen-charged samples was studied. However, the whole of diffusion coefficients did not agree well with each other, especially at lower temperatures, from the viewpoints of both an absolute value and the temperature dependence.

From the standpoint of the large scatter of diffusivity reported, we have expected that the experimental data would be characterized in general by the increase of apparent activation energy corresponding to a slope of the linear part on the Arrhenius plot, and by gathering of diffusivity at about 900 K near the melting point of aluminum.

The increasing process of activation energy implied that the logarithm of pre-exponential factor ($\log D_0$) increased correspondingly with the activation energy (Q). Watanabe *et al.*⁽¹⁷⁾ pointed out recently this phenomena for the Al-H system, as for other metals of α -Fe, Ni, Cu and graphite, by way of the "compensation effect" which was originally deduced from a reaction in heterogeneous catalysis. They proposed a model for the large scattering of hydrogen diffusivity in aluminum, which was the two channels of the diffusion mechanism being constructed from a normal lattice diffusion and a fast diffusion along the grain boundary⁽¹⁵⁾.

Anyway, what is the most important reason for the

large scattering and/or characteristic increase of activation energy of hydrogen diffusion as shown in Fig. 1? The major purpose of this study is to answer this question, mainly from a viewpoint of the grain boundary effect which should play a great role in a process of diffusion of hydrogen.

II. Experimental

To make clear the grain boundary effect on hydrogen diffusivity, it was necessary to study the grain size dependency of hydrogen diffusivity and solubility. Two kinds of samples of ND and AM0 which were prepared from 4N (99.99 mass%) aluminum. Sample ND was remelted and solidified uni-directionally in a pure nitrogen

Fig. 1 Comparison of hydrogen diffusivity in pure solid aluminum.

* Department of Materials Science, Faculty of Engineering, Ibaraki University, Hitachi 316, Ibaraki, Japan.

Table 1 Hydrogen diffusivity data reported so far in pure solid aluminum.

(Ref. No) Abbrev. (Year)	Method	Purity	Initial gas ($10^{-5} \text{ m}^3 \text{ kg}^{-1}$)	Grain diameter (mm)	Temperature (K)	D_0 (m^2/s)	Q (kJ/mol)
[Hydrogen]							
(1) RT (1955)	Desorption (99.994 mass%)	4N4	0.32		693–793	12	140
(2) EP (1957)	Desorp.	2N5			743–863	2.1×10^{-5}	45.6
(3) EHP (1961)	Desorp.	4N			633–873	1.1×10^{-5}	40.9
(4) MH (1967)	Desorp.	4N	0.76		823–913	2×10^{-6}	52.3
(5) PK1 (1977)	Desorp.	2N8	0.5	0.1	723–863	2.5×10^{-2}	90
(6) PK2 (1983)	Desorp.	5N		1–3	720–860	2×10^{-5}	41
(7) PK3 (1981)	Desorp.	5N/H ₂ O			723–863	1.27×10^{-3}	71
(8) IIH (1979)	Desorp.	4N	0.05	10–20	573–923	4.6×10^{-6}	37
(9) OPS (1982)	Desorp.	4N5		4	773–898	1.01×10^{-5}	47.7
(10) HK1 (1983)	Permeation	6N			598–673	2.6×10^{-5}	58.9
(10) HK2 "	"	(Zone refined)			"	2.1×10^{-5}	59.8
(11) IM (1986)	Electrolytic	4N		3	285–328	9.2×10^{-5}	55.3
(12) CY (1987)	Electr.	Pure Al,			room temp	$\cdots D (\text{m}^2/\text{s}) = 10^{-13}$	
(13) CB (1984)	Electr.	Vapor deposited		$0.5\text{--}1 \times 10^{-3}$	rt	$\cdots D (\text{m}^2/\text{s}) = 10^{-19} \sim 10^{-20}$	
[Calculated on vacancy trap]							
(14) L (1988)	Lattice diffusion				600–933	8×10^{-5}	50.2
[Deuterium]							
(15) STIAW (1990)	Desorp. *(original value)	5N5		0.6	293–343	7.6×10^{-7} *(4.2)	78 (115)
[Tritium]							
(16) NAT1 (1981)	Desorp.	2N5 Recoil-injected			338–472	2×10^{-7}	42.6
NAT2 (1981)	Desorp.	2N5 Thermally-doped			423–796	9×10^{-7}	51.9

gas flow. Therefore, there were no grain boundaries in the cylinder sample ND of 20 mm diameter and 25 mm length, we denoted that an average grain size as the diameter was greater than 25 mm. We supposed that sample ND was actually a single crystal. Sample AM0 was melted and cast in air, which had a smaller grain diameter of about 4 mm. The specific gravity was measured by the Archimedes' method, and the ingot soundness was estimated from the lower deviation from the specific gravity of 2.700 for solid pure aluminum. Because the specific gravity of both samples were the same as for a void-free aluminum melted in a vacuum of 2.700, sample AM0 and of course sample ND contained no voids.

Measurements of hydrogen diffusivity and solubility were performed by a vacuum hot-extraction method which had been explained in detail elsewhere⁽⁸⁾. Briefly speaking, the apparatus had four sections of (1) extraction, (2) pressure measurement, (3) evacuation and (4) hydrogen analyzing with a palladium tube. Degassing from as-cast samples and extraction from thermally hydrogen-charged samples were followed by putting the samples into a heated graphite crucible set in an evacuated extraction section having a constant known volume. By analyzing of the extraction process, we measured diffusion coefficient (D) and solubility (S) of hydrogen.

III. Results and Discussion

Diffusivity and solubility of hydrogen were measured for two samples of ND (single crystal; no grain boundary) and AM0 (finer grain size), in the same way as our previous studies⁽¹⁸⁾ for two samples of VM and AM⁽⁸⁾ being actually void-free, and for three samples of AS, AB1 and AB2⁽¹⁸⁾ containing some voids, and all the results were examined comparatively with each other.

All of our diffusivity and solubility data were summarized in Table 2 with the experimental conditions, and the temperature dependence was illustrated in Fig. 2 for diffusivity and in Fig. 3 for solubility. As seen in Fig. 2, hydrogen diffusivity had a linear temperature dependency in the Arrhenius plot and it was characterized by an increase of apparent activation energy having a fixed diffusivity at about 900 K nearby the melting point of aluminum. The activation energy increased with increasing number of voids. There was, however, still more scattering in diffusivity between the samples with practically no voids, where the diffusivity might be controlled by some other factors except for the void-trapping which had been studied by us⁽¹⁸⁾.

On the other hand, the results of hydrogen solubility was somewhat different from that of diffusivity. As shown in Fig. 3, solubility was increased with the number of voids which contained hydrogen gas inside, but there

Table 2 Hydrogen diffusivity and solubility in high purity solid aluminum (4N=99.99 mass%) with various grain size and voids.

Sample	VM	ND	AM0	AM	AS	AB1	AB2
Shape of grain	columnar	single crystal	granular	granular	granular	granular	granular
Size of grain dia. average (mm)	10–20 15	>25	1–7 4	1–3 2	1–5 3	1–5 3	2–6 4
Specific Gravity	2.700	2.700	2.700	2.699	2.695	2.687	2.695
Voids?	No	No	No	(No)	Yes	Yes	Yes
Diameter of void (μm)					50–100	50–100	50–100
Number of void (m^{-3})					8×10^9	2.3×10^{10}	1.5×10^{10}
Void volume %	0	0	0	(0.04)	0.17	0.50	0.19
Refer.	(8) IIH	present study	present study	(8) IIH	(18) II	(18) II	(18) II
[Diffusivity] $D = D_0 \exp(-Q/RT)$							
Temp. (K)	573–923	473–903	573–903	623–913	623–903	623–903	573–903
D_0 (m^2/s)	4.58×10^{-6}	9.53×10^{-6}	1.52×10^{-5}	2.11×10^{-4}	1.54×10^{-3}	4.22×10^{-2}	6.00×10^{-3}
Q (kJ/mol)	37.0	44.3	53.4	67.0	81.2	106.9	88.7
[Solubility] $S = A \exp(-B/T)$							
Temp. (K)	723–923	723–903	773–873	773–913	623–903	673–903	623–903
A ($10^{-5} \text{ m}^3 \text{ kg}^{-1} \text{ atom}^{-0.5}$)	164	42.4	124	164*	1.445	2.831	4.634
B (K)	7690	6580	7570	7690*	2970	3017	3938

*There are two additional points for AM of 0.0059 at 723 K and 0.0066 at 673 K.

Fig. 2 Arrhenius type plots of hydrogen diffusivity.

Fig. 3 Arrhenius type plots of hydrogen solubility.

Table 3 Some trapping sources for hydrogen in metals.

A: Intrinsic or chemical trapping ⁽¹¹⁾⁽²⁰⁾	
1. Hydride formation	
2. Isotopic mass effect of H, D and T	
3. Diffusion mechanisms for deviation from Arrhenius relation	
4. Dual site occupation of O- and T-site	
5. Lattice dilatation due to thermal expansion and vacancy formation	
B: Extrinsic or physical trapping ⁽²¹⁾⁽²²⁾	
B1. Point defect (zero dimension), short-range and isolated type	
1. Vacancy	3. Substitutional impurity atom
2. Interstitial impurity atom	4. Self-interstitial
B2. Line defect (1st dimension), long-range and continuous type	
1. Dislocation	4. Long and slender (linear) inclusion or particle
2. Moving dislocation	
3. Tangled dislocation	
B3. Surface defect (2nd dimension), long-range and continuous type	
1. Surface (oxide layer)	3. Grain boundary
2. Interface (particle or inclusion with matrix)	
B4. Volume defect (3rd dimension), short-range and isolated type	
1. Vacancy cluster	4. Micro-void or porosity
2. Impurity cluster	5. Cleavage or crack
3. Inclusion or particle	6. Strain or stress field

were almost no differences between void-free samples.

By referring to the literature^{(11)(20)–(22)}, some trapping sources for hydrogen in metals were summarized in Table 3 with two groups of A: intrinsic or chemical trapping⁽¹¹⁾⁽²⁰⁾, and B: extrinsic or physical trapping⁽²¹⁾⁽²²⁾.

The factors of group A in Table 3 had nearly no influences on the hydrogen diffusion in aluminum⁽¹¹⁾. It was not clear an isotopic mass effect (A-2), especially at lower temperature. The isotopic mass effect on the diffusion of hydrogen isotopes must be studied in the sample with the same level to the amount of other defects as trapping sources.

In the present study, the high-purity aluminum sample was not deformed (as cast or annealed), shaped in cylindrical and massive sample with a small surface area per unit volume, and treated in a relatively high temperature range of 600–900 K. Almost all sources of group B in Table 3 might be ignored for the factors of hydrogen trapping. The trapping effect of thermal-equilibrium vacancy⁽¹⁴⁾ (B-1-1) was not so large even at higher temperature as shown by a broken line in Fig. 1. After all, only two sources were survived now for hydrogen trapping factor: one was grain boundary (B-3-3) for the polycrystal sample and another was microvoids (B-4-4) for the sample usually melted and cast in air.

We had already investigated for a large scattering of hydrogen diffusivity based on a hydrogen gas trapping in void as gas defects in solid pure aluminum⁽¹⁸⁾, and we concluded that an increasing of void, in which hydrogen gas was trapped, brought a decreasing of diffusivity and increasing of solubility of hydrogen. But on that time, we did not worry about any other factors, except for voids,

to control the hydrogen diffusivity or solubility in pure solid aluminum.

It had been known that the grain boundary had a pervasive role⁽²⁰⁾⁽²¹⁾ as traps and/or short-circuits for diffusing species, but its details were not so certain, as shown in follows. Baskes and Vitek⁽²³⁾ examined that the defect-free or clean grain boundary in nickel played a role of trapping of helium, but it did not act as trapping site for hydrogen. Brass *et al.*⁽²⁴⁾ observed a short-circuit effect of grain boundary in the first stage of permeation and/or degassing in pure nickel foil. Yao and Cahoon⁽²⁵⁾ predicted theoretically no effects of the enhanced grain boundary transport of hydrogen with the grain size of greater than 10 μm , and however, they⁽²⁶⁾ measured unexpectedly a trapping effect by grain boundary in two samples of grain sizes of 10 μm and 150 μm .

Recently Outlaw *et al.*⁽⁹⁾ measured hydrogen diffusivity and solubility for the “large grain” aluminum, having an average grain diameter of 4 mm, in which their diffusivity and solubility were smaller respectively of one-sixths and two-sixths than the values reported previously by Eichenauer *et al.*⁽²⁾⁽³⁾ They⁽⁹⁾ expected that the grain size of Eichenauer’s sample must be smaller than their own, and they explained that their lower solubility of hydrogen was given by decreasing of grain boundary trapping, and that their lower diffusivity of hydrogen was given by the decreasing of fast diffusion along grain boundary. This was the first report for us which proposed a possibility of grain boundary effect in both terms of “fast diffusion” and “trapping” of grain boundary in aluminum.

Location and/or distribution of trapped hydrogen had been often studied by the method of electron-microautoradiography. Saitoh *et al.*⁽²⁷⁾ investigated the tritium behavior in Al–Si–Mg alloy by the method. They had some very interesting facts that the dislocation was capable of being trapping site as well as short-circuit path, and that the clean and not precipitated grain boundary itself was capable of short-circuit path but did not act as trapping site.

Before we are going to stress on a role of grain boundary to hydrogen behavior in aluminum, it is, however, interesting to note the way of temperature dependency of the apparent hydrogen diffusivity in the Arrhenius plot.

A change of temperature dependency of diffusivity in the Arrhenius plot, so-called the “compensation effect”, was clearly shown in Fig. 4, where the data for all samples in spite of with or without void were just on a line which was obtained by us for hydrogen diffusion in pure aluminum and Al–Cu alloys⁽¹⁹⁾. Watanabe *et al.*⁽¹⁵⁾⁽¹⁷⁾ had proposed three different interpretations for the “compensation effect” on hydrogen diffusion in many metals. They⁽¹⁵⁾ selected a mechanism of double diffusion channels being in parallel and/or series on the basis of their own data for deuterium diffusion in aluminum. And they⁽¹⁵⁾ concluded that the large scatter of hydrogen diffusivity at low temperature was depended both upon the lowest diffusivity of hydrogen in lattice of grain and the highest diffusivity of hydrogen enhanced diffusion

Fig. 4 Linearity between $\log D_0$ and Q , so-called “compensation effect”.

along grain boundaries. The mechanism of “compensation” must be examined in detail experimentally and theoretically.

To answer why the scattering of hydrogen diffusivity in aluminum was so large, we noticed two kinds of effects by grain boundary itself. One of them was an enhancemental effect on hydrogen diffusion along grain boundary, the other was a hydrogen trapping effect by some nodes or joints as the junction-points at the grain boundary network. As the grain size was decreasing from infinity for a single crystal, the hydrogen mobility was increased with an area of grain boundary by an enhanced diffusion effect along grain boundaries. But the sample with a smaller grain size had many more nodes or junctions of grain boundary which would trap some hydrogen atoms and would suppress a hydrogen mobility. As a result of these two contrary effects of an enhancement and a trapping, the hydrogen diffusivity had a maximum at some intermediate grain size. We indicated this effect in Fig. 5 as the grain diameter dependence of hydrogen diffusion coefficients at two temperatures of 773 and 573 K. We called this as “grain boundary cross effect” on hydrogen diffusivity in pure solid aluminum. A group of sample with some voids shown by symbol $\odot$ in Fig. 5 at 573 K represented a lower diffusivity than that of sample group with no voids by symbol $\circ$. This was a good evidence for void trapping effect at lower temperature⁽⁸⁾⁽¹⁸⁾ by which it was brought a suppressed diffusion of hydrogen in aluminum with some voids. Figure 6 was a schematic representation of the “grain boundary cross effect” on the hydrogen diffusivity, being mainly based

Fig. 5 Grain boundary effect of the hydrogen diffusivity.

Fig. 6 A model for the “grain boundary cross effect” on the hydrogen diffusivity.

on an arrangement of grain boundary, which had two contrary effects of (a) an enhanced and long-range diffusion along a straightforward grain boundary and (b) a suppressed diffusion by trapping of hydrogen at grain boundary nodes.

Figure 7 was for showing that the more larger solubility was obtained apparently for the more total volume of voids in sample, but solubility of sample group with no voids were independent of grain size. We concluded that

Fig. 7 Grain boundary effect of the hydrogen solubility.

grain boundary in aluminum had a strong and complex effects on hydrogen diffusivity, but it had no effects on hydrogen solubility, and it was not very large the total number of hydrogen atoms trapped at grain boundary nodes.

IV. Summary

Both solubilities and diffusion coefficients of hydrogen in pure solid aluminum having different grain sizes were measured by means of a thermal gas charging and vacuum hot extraction method.

(1) Temperature dependency of hydrogen diffusivity was followed by a linear rule in the Arrhenius type plot, in which the lines were intersected at about 900 K.

(2) Logarithm of pre-exponential factor ($\log D_0$) was closely on a straight line to activation energy (Q) for hydrogen diffusion, being called "the compensation effect" on the diffusion process.

(3) Grain boundary had two kinds of effect on a hydrogen mobility. One was a fast or enhanced diffusion along grain boundaries, being notable for larger grain sized samples nearly single crystal. Another was a suppressed diffusion by trapping of hydrogen at grain boundary nodes, which might be remarkable for samples with

smaller grain sizes. This is called "the grain boundary cross effect".

(4) The grain boundary had no effect on hydrogen solubility in pure solid aluminum, in spite of its large effect on hydrogen diffusivity.

REFERENCES

- (1) C. E. Ransley and D. E. J. Talbot: J. Inst. Metals, **84** (1955-56), 445.
- (2) W. Eichenauer and A. Pebler: Z. Metallk., **48** (1957), 373.
- (3) W. Eichenauer, K. Hattenbach and A. Pebler: Z. Metallk., **52** (1961), 682.
- (4) S. Matsuo and T. Hirata: J. Japan Inst. Metals, **31** (1967), 590.
- (5) K. Papp and E. Kovacs-Csetenyi: Scripta Metall., **11** (1977), 921.
- (6) K. Papp and E. Kovacs-Csetenyi: DIMETA 2, the *Proceedings of the International Conference on Diffusion in Metals and Alloys*, held at Tihany, Hungary, (1982), p. 450.
- (7) K. Papp and E. Kovacs-Csetenyi: Scripta Metall., **15** (1981), 161.
- (8) M. Ichimura, M. Imabayashi and M. Hayakawa: J. Japan Inst. Metals, **43** (1979), 876.
- (9) R. A. Outlaw, D. T. Peterson and F. A. Schmidt: Scripta Metall., **16** (1982), 287.
- (10) H. Hashimoto and T. Kino: J. Phys. F., Met. Phys., **13** (1983), 1157.
- (11) T. Ishikawa and R. B. McLellan: Acta Metall., **34** (1986), 1091.
- (12) Y. Chu and H. Yin: *10th International Congress on Metallic Corrosion*, Vol. 3: Sessions 10-13, Madras, India, 7-11 Nov. (1987).
- (13) W. Y. Choo and I. M. Bernstein: Met. Trans. A, **15A** (1984), 1953.
- (14) S. Linderth: Phil. Mag. Letters, **57** (1988), 229.
- (15) M. Sonobe, S. Toda, S. Ikeno, K. Ashida and K. Watanabe: J. Nucl. Mater., **175** (1990), 47.
- (16) M. Nakashima, Y. Aratono and E. Tachikawa: J. Nucl. Mater., **98** (1981), 27.
- (17) K. Watanabe, K. Ashida and M. Sonobe: J. Nucl. Mater., **173** (1990), 294.
- (18) M. Ichimura and M. Imabayashi: J. Japan Inst. Metals, **44** (1980), 1045.
- (19) M. Ichimura, Y. Sasajima and M. Imabayashi: J. Japan Inst. Light Metals, **39** (1989), 639, *ibid.*, **40** (1990), 95.
- (20) J. Philibert: *Diffusion in Materials*, Ed. by A. L. Laskar *et al.*, Kluwer Academic Publishers, Netherlands, (1990), p. 1.
- (21) C. A. Wert: *Hydrogen in Metals II, Application-Oriented Properties*, Ed. by G. Alefeld and J. Volkl, Springer-Verlag, (1978), p. 305.
- (22) Y. Iijima and K. Hirano: Bull. Japan Inst. Metals, **14** (1975), 559.
- (23) M. I. Baskes and V. Vitek: Met. Trans. A., **16A** (1985), 1625.
- (24) A. M. Brass, A. Chaufreau and J. Chene: *Diffusion in Materials*, Ed. by A. L. Laskar *et al.*, Kluwer Academic Publishers, Netherlands, (1990), p. 652.
- (25) J. Yao and J. R. Cahoon: Acta Metall. Mater., **39** (1991), 111.
- (26) J. Yao and J. R. Cahoon: Acta Metall. Mater., **39** (1991), 119.
- (27) H. Saitoh, Y. Iijima and K. Hirano: J. Japan Inst. Light Metals, **36** (1986), 286.