ELSEVIER

Journal of Alloys and Compounds 330–332 (2002) 649–653

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Characterization of the charging techniques used to introduce hydrogen in aluminum

C.E. Buckley[a,]*, H.K. Birnbaum[b]

[a]The Department of Applied Physics, Curtin University of Technology, Perth, 6845 WA, Australia
[b]Materials Research Laboratory, University of Illinois, Urbana, IL 61801, USA

Abstract

Aluminum foils and single crystals of varying thickness and purity were charged with hydrogen using gas plasma, electrochemical and chemical methods. The concentrations of hydrogen introduced were monitored by gas extraction and prompt γ-activation analysis measurements. X-ray diffraction measurements indicated that within experimental error there was either a small lattice contraction or a zero change in lattice parameter after charging. It was found that during cathodic and chemical charging an $Al(OH)_3$ layer formed on the surface. Extensive experiments revealed that unless the surface layer formed during the charging process was removed, the concentration of H measured with either analysis method was erroneously high. The plasma charged samples do not form an $Al(OH)_3$ layer on the surface, but instead form H–vacancy complexes at the surface which diffuse into the volume and then cluster to form H_2 bubbles. The structure of the hydrogen solutes introduced by the charging methods is discussed and the diffusivity of a hydrogen–vacancy complex at 300 K is estimated.

Keywords: Metal hydrogen; Aluminium; Hydrogen charging; Hydrogen–vacancy complex, Hydrogen bubbles

1. Introduction

Although studies of the solubility of hydrogen in molten and solid aluminum in the temperature range of 573–1473 K [1–5] have been carried out, little is known of the hydrogen solubility and structure in the vicinity of room temperature. The diffusivity and permeability of hydrogen in aluminum has been studied in the temperature range 285–328 K [6], but no independent measurement of the solubility was made. Recent measurements of the solubility of hydrogen in aluminum [7] at room temperature determined that very large concentrations (>1000 appm) of hydrogen could be introduced using electrochemical, chemical and ultrasonic water bath charging techniques at room temperature. After charging, X-ray diffraction showed that the very high hydrogen concentrations resulted in either a small decrease or a zero change in lattice parameter. This is in direct contrast to observations in other fcc metals, where a considerable lattice expansion of approximately 2.9 $Å^3$ per H atom is exhibited [8].

In the present paper, high concentrations of hydrogen were introduced into aluminum at room temperature using electrochemical, chemical and gas plasma methods. The concentrations were monitored by gas extraction, lattice parameter, and prompt γ-activation analysis (PGAA). The structure of the hydrogen solutes were investigated and the diffusivity of the hydrogen–vacancy complexes at 300 K were estimated.

2. Experimental procedures

For the experiments described in this paper and in Ref. [7], polycrystalline specimens were cut from aluminum having purities of 99.99% (thickness of 130 μm (series A)), 98.6% (thickness of 50 μm (series B)), and 99.999% (thicknesses of 100 μm (series C) and 1000 μm (series D)). For small angle neutron scattering (SANS) experiments specimens were cut from single crystals grown from the 99.999% aluminum in vacuum by a Bridgman technique (series E and F). The cutting was by spark erosion and was followed by careful polishing to ~1000-μm thick so as to minimize the damage to the surfaces. SANS experiments also utilized stacks of the 130-μm foils (series A) to obtain sufficient material for the neutron scattering. All specimens were given a final anneal at 833 K in a vacuum of 10^{-4} Pa.

---

*Corresponding author.
E-mail address: rbuckley@cc.curtin.edu.au (C.E. Buckley).

0925-8388/02/$ – see front matter
PII: S0925-8388(01)01496-7

Hydrogen charging was carried out using three methods — cathodic charging in H_2SO_4 or HCl, using $NaAsO_2$ as a hydrogen recombination ‘poison,’ by etching in NaOH (pH 10–12) containing $NaAsO_2$ as a hydrogen recombination ‘poison,’ and by immersion in a H_2 gas plasma at voltages ranging from 0.5 to 1.2 keV. While each of the three charging methods produced high concentrations of hydrogen in the aluminum, they differed in several important respects. The electrolytic charging utilized a Pt anode and current densities of 1–200 mA cm^{-2}. During the electrolytic charging an $Al(OH)_3$ layer formed on the aluminum surface. It could be removed by mechanically wiping the surface immediately after electrochemical charging. Unless it was removed, spurious concentrations of hydrogen were measured during analysis as discussed below.

Hydrogen concentrations in specimen Series A and B obtained using the H_2 gas plasma method at current densities from 7×10^{-4} to 0.75 mA cm^{-2} and charging times range from 357 to 4320 min were studied. It was found that at H ion current densities >0.5 mA cm^{-2}, H concentrations >1000 appm were obtained as measured by both the gas extraction and PGAA methods. In some cases concentrations approaching 3000 appm were obtained using charging times sufficient to allow equilibration of H throughout the foil thickness. The surfaces after plasma charging were clean and did not have an $Al(OH)_3$ layer.

The hydrogen distributions through the specimen thicknesses during charging by the various methods were estimated from the hydrogen diffusivity, 2×10^{-14} m^2 s^{-1} [6], at the charging temperature. As shown in Table 1, for the charging times used, a uniform H distribution was attained in specimen series A, B and C, was not attained in specimen D, and was almost attained in specimen series E and F. For the gas plasma method, the distribution of the H introduced below the surface by the plasma was determined by the TRIM [9] program and the average depth of implantation was calculated to be 194 Å.

The concentration of hydrogen in the aluminum was determined using two methods, both of which agreed well for comparably charged specimens. The first utilized a high temperature vacuum extraction technique with the amount of H_2 released being determined by gas chromatography. The second method employed prompt γ-activation analysis (PGAA) where the intensity of emission of γ-rays of 2223.23 keV energy measures the amount of hydrogen in the sample [10]. The sensitivity of both methods was approximately 50 appm. Extensive experiments revealed that unless the surface layer formed during cathodic charging was removed, the concentration of H measured with either analysis method was erroneously high. The surface layer was found to be $Al(OH)_3$ and on heating for the gas chromatography measurements the hydroxide decomposed to Al_2O_3 and H_2 resulting in a erroneously high measured concentration of hydrogen. The PGAA method also gave anomalous high values of H/M as it measures the total H concentration regardless of whether the hydrogen is present as solute H or in $Al(OH)_3$. Table 2 compares the H concentration of hydrided polycrystalline foils with different surface treatments after charging. Samples 1a, 1b, 3a and 4a had their surfaces cleaned after charging and the surfaces of samples 2a, 2b, 3b and 4b were not cleaned after charging. Comparisons between samples 1a and 2a, 1b and 2b, 3a and 3b, and 4a and 4b show that the samples that had the $Al(OH)_3$ layer removed before analysis had values of H/M an order of magnitude less than those samples which had no surface cleaning.

Experiments were also conducted to estimate the maximum amount of H introduced using the cathodic charging

Table 1

Distance diffused by H and vacancies during the H charging times and the times required to achieve a homogeneous distribution of H and vacancies calculated using the measured diffusivities [6,16,18]

Specimen series	Charging method and time (min)	Vacancy diffusion distance during H charging (μm)	Hydrogen diffusion distance during charging (μm)	Time required for a homogeneous vacancy distribution (min)	Time required for a homogeneous H distribution (min)
99.99% purity foil, 130-μm thick (Series A)	4.56×10^{3} (Plasma)	21	148	4.20×10^{4}	8.80×10^{2}
98.6% purity foil, 50-μm thick (Series B)	1.44×10^{3} (Plasma)	12	83	2.55×10^{3}	1.30×10^{2}
99.999% purity foil, 100-μm thick (Series C)	1.44×10^{3} (Cathodic)	12	83	2.49×10^{4}	5.21×10^{2}
99.999% purity foil, 1000-μm thick (Series D)	2.88×10^{3} (Chemical)	17	120	2.49×10^{6}	5.21×10^{4}
99.999% single crystal 1000-μm thick (Series E)	2.86×10^{4} (Plasma)	54	370	2.49×10^{6}	5.21×10^{4}
99.999% single crystal 1000-μm thick (Series F)	3.13×10^{4} (Plasma)	56	390	2.49×10^{6}	5.21×10^{4}

Table 2
A comparison of the H concentrations measured for cathodically charged aluminum (Series B) with the surface film removed and present for the gas chromatographic (GC) and prompt γ-activation analysis (PGAA) methods of H/M analysis

Sample	Cathodic current density (mA cm^{-2})	Charging time (min)	H/M (appm) and method of analysis	Surface treatment after charging
1a	20	24	250±50 (GC)	Cleaned
2a	20	24	4760±50 (GC)	Not cleaned
1b	20	24	0±50 (PGAA)	Cleaned
2b	20	24	4600±50 (PGAA)	Not cleaned
3a	50	3935	570±50 (GC)	Cleaned
3b	50	1898	11740±50 (GC)	Not cleaned
4a	50	60	210±50 (GC)	Cleaned
4b	50	60	2620±50 (GC)	Not cleaned

method. Table 3 shows the H concentrations for 11 samples, charged for varying times and current densities. All of these samples had the $Al(OH)_3$ layer removed after charging. The highest concentration was found to be 770 appm; consistent with the conclusion that the highest H concentrations in the cathodic charged specimens in Table 2 (2a, 2b, 3b and 4b) are mainly due to the $Al(OH)_3$ layer on the surface.

Lattice parameter measurements were made immediately after charging using step scans through the X-ray peaks obtained with Cu Kα radiation. The lattice parameters calculated from lines at various Bragg angles, θ, were extrapolated versus $\cos^2\theta/\sin\theta$ to increase the precision of measurement. The precision of the change in lattice parameter, $\delta a/a_0$ was estimated to be 5×10^{-5} from the standard deviation of repeated measurements (including repeated placement of the specimen in the specimen holder) on a reference specimen. For the 99.99% pure aluminum samples, which were hydrogen plasma charged, $\delta a/a_0$ was measured for the (400) peak only, due to the samples being heavily textured.

Table 3
Hydrogen concentrations measured in hydrided aluminum foil (98.6% pure), where the $Al(OH)_3$ layer was removed immediately after charging

Sample–foil 98.6% Purity	J (mAcm^{-2})	Charging time (min)	H/M (appm) and method of H/M analysis (±50 appm)
1	100	6911	770 (G/C)[a]
2	500	29	680 (G/C)
3	30	498	580 (G/C)
4	20	1392	520 (G/C)
5	47	312	510 (G/C)
6	40	1649	500 (G/C)
7	3	1352	450 (G/C)
8	20	923	420 (G/C)
9	0.5	1555	390 (G/C)
10	20	302	330 (G/C)
11	Not hydrided	N/A	170 (G/C)

[a] G/C denotes that the solubility for that particular sample was measured using gas chromatography.

3. Results and discussion

Introduction of hydrogen into the lattice of fcc solids generally results in a considerable lattice expansion [1] with almost all systems exhibiting a volume expansion of $\delta V_H = 2.9$ Å^3. For the atomic volume (Ω) of aluminum this corresponds to $\delta V_H/\Omega = 0.175$ per hydrogen atom. Table 4 shows the calculated lattice parameter change $(\delta a/a_0)_H$, using the measured solute hydrogen concentrations for each of the charging conditions used. Lattice *expansions* in the range of $+3\times10^{-5}$ to $+2\times10^{-4}$ are expected for the measured hydrogen concentrations. In contrast, the measured values of $\delta a/a_0$ (Table 4) are negative, i.e. a *contraction* of the lattice occurred indicating that the solute hydrogen induced lattice expansion is significantly less in aluminum than in other metals.

These results can be accounted for by the formation of a lattice vacancy at the surface accompanying the introduction of a H solute followed by the diffusion of the H–vacancy complex into the volume. In this model, the vacancies are formed at the external surfaces and the additional lattice sites formed are introduced at the external surfaces rather than at internal vacancy sources. In the situation where the H–vacancy complexes remain dispersed as individual defects, the volume change is:

$$\frac{\delta a}{a_0} = \frac{\delta L}{L_0} = \frac{1}{3}\left(\frac{\delta V}{V_0}\right) = \frac{1}{3}\left(C_H\frac{\delta_H}{\Omega} + C_V\frac{\delta_V}{\Omega}\right) \qquad (1)$$

where C_V is the concentration of vacancies and $\delta_V/\Omega = -0.35$ is the lattice relaxation due to a vacancy in aluminum [11]. From Eq. (1), the values of C_V and C_V/C_H can be calculated and are shown in Table 4.

For the plasma charged sample (series A) an independent determination of C_V was made using precision density measurements, and the ratio of C_V/C_H calculated from this data is 24 times greater than the calculated ratio of C_V/C_H determined from Eq. (1). The calculated ratio (from Eq. (1)) of C_V/C_H assumes that the H–vacancy complexes remain dispersed throughout the lattice as individual defects. However it is known experimentally [12–15] from

Table 4
Values for the concentrations of hydrogen, C_H obtained on charging; $\delta a/a_0$ calculated from C_H; the experimental values of $\delta a/a_0$; the calculated C_V (Eq. 1); C_V/C_H (calc.) and C_V/C_H (expt.)

Charging conditions	C_H (appm)	Calculated values of $\delta a/a_0$ (H only)	$\delta a/a_0$ (expt.) $\pm 5\times10^{-5}$	C_V (calc.)	C_V (expt.)	C_V/C_H (calc.)	C_V/C_H (expt.)
Cathodic charging:							
1N $H_2SO_4 + NaAsO_4$, pH 1; 35°C, 50 mA cm^{-2} (Series C)	700	$+4.1\times10^{-5}$	-1.7×10^{-4}	1.8×10^{-3}	N/A	2.6	N/A
Chemical charging:							
1N NaOH; pH 12; $t=24$ h (Series C)	600	$+3.5\times10^{-5}$	-3.3×10^{-4}	3.1×10^{-3}	N/A	5.2	N/A
Plasma charging:							
$T=76$ h (Series A)	2880	$+1.7\times10^{-4}$	$+7\times10^{-6}$	1.4×10^{-3}	3.3×10^{-2}	0.48	16
$T=24$ h (Series B)	1300	$+7.6\times10^{-5}$	-4×10^{-5}	9.9×10^{-4}	N/A	0.76	N/A

small and ultra small angle neutron scattering (SANS and USANS), inelastic neutron scattering (INS), and scanning and transmission electron microscopy measurements (SEM and TEM) that the H–vacancy complexes cluster together to form H_2 bubbles. The resulting internal pressure can be reduced as the compressive field of the H_2-bubbles will attract extra vacancies created by the initial 1-keV ions [13–15]. The extra vacancies increase the volume of the bubbles, giving rise to the experimentally determined large value of C_V/C_H. Therefore the large difference between the calculated and experimental value of C_V/C_H for the series A sample can be attributed to the experimental observation that in the plasma charged Al, H is in the form of H_2 bubbles, and not as individual dispersed H–vacancy defects.

The nature of the hydrogen and vacancies in the cathodic and chemically charged samples (series C) have not been investigated using the SANS, SEM, TEM and INS techniques, but the negative relative change in lattice parameter suggests that H–vacancy complexes are formed from these charging processes. Whether these complexes cluster to form H_2-bubbles or remain as dispersed H–vacancy complexes cannot be verified without additional experimental information (i.e. SEM, TEM, INS and SANS). In the cathodic and chemically charged specimens it is expected that the H is also in the form of bubbles, but that these form only from the H–vacancy complexes, as there is no source of additional vacancies.

The diffusivity of a vacancy and hydrogen in aluminum is given by Eqs. (2) and (3):

$$D_V = D_0^V \exp\left(-E_D^V/kT\right) \tag{2}$$

$$D_H = D_0^H \exp\left(-E_D^H/kT\right) \tag{3}$$

where $D_0^V = 1.1\times10^{-5}$ m^2 s^{-1} [16,17] is the vacancy diffusion prefactor, $D_0^H = 9.2\times10^{-5}$ m^2 s^{-1} [6] is the hydrogen diffusion prefactor, $E_D^V = 0.62$ eV [16,18] is the vacancy diffusion activation energy, and $E_D^H = 0.57$ eV [6] is the hydrogen diffusion activation energy at $T = 300$ K. From D_V and D_H, the time for hydrogen (t_H) and a vacancy (t_V) to achieve a homogeneous distribution in the charged foils is calculated and presented in Table 1. The 50-, 100- and 130-μm thick foils (series A, B and C) are charged long enough for the hydrogen to reach a homogeneous distribution throughout the sample. The 1000-μm thick foils and single crystals have non-equilibrium H distribution. If the vacancy mobility were not affected by the presence of H, all samples would have an inhomogeneous vacancy distribution. Although the bubbles are distributed inhomogeneously throughout the bulk, they were observed throughout the volume of the 130-μm foils (i.e. at all depths) for charging times of the order of 4.56×10^3 min (Table 1) at 300 K. From these results, the diffusivity of the H–vacancy complex can be estimated to be 3.9×10^{-15} m^2 s^{-1} at 300 K.

4. Conclusions

Hydrogen concentrations of the order of 1000 appm can be introduced into aluminum at room temperature using electrochemical and chemical charging, but care must be taken to remove the $Al(OH)_3$ layer immediately after electrochemical charging to ensure a correct solubility measurement.

Hydrogen concentrations of the order of 3000 appm can be introduced by exposing the aluminum to a low energy H_2 gas plasma. Since this method does not produce an $Al(OH)_3$ layer on the surface of the aluminum it is the most reliable method of introducing high H concentrations into aluminum at room temperature.

Either a small contraction or a zero change in the lattice parameter results when high H concentrations are introduced into the aluminum matrix. This is consistent with the formation of H–vacancy complexes at the Al surface, when H is introduced. The diffusing species is suggested to be the H–vacancy complex. The diffusivity of this complex at 300 K for the plasma charged samples is estimated to be $D_{\mathrm{H-V}} = 3.9 \times 10^{-15}$ m^2 s^{-1}.

Acknowledgements

This research was sponsored by US Department of Energy grant DEFG02-96ER45439. We would also like to thank John Barker and Rick Paul from The National Institute of Standards and Technology (NIST) for the PGAA experimental results. C.B was the holder of a Curtin University Post Doctoral Research Fellowship for part of this research.

References

[1] C.E. Ransley, H. Neufeld, J. Inst. Met. 74 (1948) 599.
[2] M. Ichimura, H. Katsuta, Y. Sasajima, M. Imabayashi, J. Phys. Chem. Solids 49 (1988) 1259.
[3] R.Y. Lin, M. Hoch, Met. Trans. A 20A (1989) 1785.
[4] M. Ichimura, Y. Sasajima, M. Imabayashi, Mater. Trans., JIM 33 (1992) 449.
[5] M. Ichumura, Y. Sasajima, Mater. Trans., JIM 34 (1993) 404.
[6] T. Ishikawa, R.B. Mclellan, Acta Met. 34 (1986) 1091.
[7] H.K. Birnbaum, C.E. Buckley, F. Zeides, E. Sirois, P. Rozenak, S. Spooner, J.S. Lin, J. Alloys Comp. 253–254 (1997) 260.
[8] H. Peisl, in: G. Alefeld, J. Volkl (Eds.), Hydrogen in Metals I, Topics in Applied Physics, Vol. 28, Springer, Berlin, 1978, pp. 53–74.
[9] J.F. Ziegler, J.P. Biersack, U. Littmark, in: J.F. Ziegler (Ed.), The Stopping and Range of Ions in Solids, Pergamon, New York, 1985, pp. 109–126.
[10] R.M. Lindstrom, J. Res. Nat. Inst. Stand. Tech. 98 (1993) 127.
[11] A. Seeger, J. Phys. F: Metal Phys. 3 (1973) 248.
[12] C.E. Buckley, H.K. Birnbaum, Physica B 241–243 (1998) 344–346.
[13] C.E. Buckley, H.K. Birnbaum, J.S. Lin, S. Spooner, D. Bellmann, P. Staron, T.J. Udovic, E. Hollar, J. Appl. Crystallogr. 34 (2001) 119–129.
[14] C.E. Buckley, in: Proc. of the 1999 Joint Conference: WASEM and AXAA Inc., Mandurah, Australia, Sept. 17–19, 1999, pp. 29–37.
[15] C.E. Buckley, H.K. Birnbaum, E. Hollar, D. Bellmann, P. Staron, T.J. Udovic. (2000) in preparation.
[16] S.M. Myers, P. Norlander, F. Besenbacher, J.K. Nørskov, Phys. Rev. B. 33 (1986) 854.
[17] N.L. Peterson, S.J. Rothman, Phys. Rev. B 1 (1970) 3264.
[18] R.W. Siegel, in: J.I. Takamura, M. Doyama, M. Kiritani (Eds.), Point Defects and Defect Interactions in Metals, North-Holland, Amsterdam, 1982, p. 533.