

Vacancy clustering in quenched Al-Li solid solution alloys studied by Doppler broadening spectroscopy

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1998 J. Phys.: Condens. Matter 10 10423

(<http://iopscience.iop.org/0953-8984/10/46/010>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.210

The article was downloaded on 14/05/2010 at 17:53

Please note that [terms and conditions apply](#).

Vacancy clustering in quenched Al–Li solid solution alloys studied by Doppler broadening spectroscopy

H P Leighly Jr† and P G Coleman‡

† Department of Metallurgical Engineering, University of Missouri–Rolla, Rolla, MO 65409, USA

‡ School of Physics, University of East Anglia, Norwich NR4 7TJ, UK

Received 30 April 1998

Abstract. The clustering of vacancies in severely quenched Al–Li solid solution alloys, with Li content between 230 and 2760 ppm, has been studied using Doppler broadening spectroscopy. The alloy samples were initially annealed at 873 K in dry air or dry, pure nitrogen. The onset temperature for vacancy clustering in samples initially annealed in air was found to be 150 ± 10 K, 40 ± 15 K lower than for the nitrogen-annealed samples. This result is consistent with the migration of divacancies, formed as a result of the significant increase in vacancy concentration caused by Li migration to, and oxidation at, the surfaces of samples annealed in air. Li–vacancy binding may also contribute, to a lesser extent, to the retardation of vacancy migration in the nitrogen-annealed samples. No dependence on Li content was seen in the results for the two sets of samples.

1. Introduction

Al–Li alloys have structural applications where higher-strength alloys having lower density and increased elastic moduli are required [1]. In such alloys, in addition to being strengthened by Li in the Al solid solution, there is always sufficient Li present for the formation of AlLi, the stable δ phase, and Al₃Li, the metastable δ' phase [2]. Both phases act as a barrier to dislocation motion.

Because of the reactivity of Li in air and its volatility at elevated temperatures, there may be significant losses of this alloying element from the surface during the heat treatment of Al–Li alloys. Papazian *et al* [3] used the nuclear reaction ${}^7\text{Li}({}^3\text{He}, \text{p}){}^9\text{Be}$ to study the depletion of Li from the surface as a function of composition, temperature and annealing atmosphere. They found severe Li depletion in the surface layers of two commercial Al–Li alloys, 8090 and 8091, after being heated in argon, dry air or wet air. The depletion extended as much as 0.4 mm from the surface of the test specimens, decreasing with increasing depth. They also observed the development of porosity at depth which they attributed to the Kirkendall effect [4], whereby Li atoms diffuse to the surface more rapidly than Al atoms are able to replace them in the crystal lattice. This results in a surplus of vacancies in the interior of the alloy which agglomerate to form voids (visible to an optical microscope at $\times 70$ magnification).

Holdway and Bowen [5] identified LiCO₃ and γ -LiAlO₂ in the oxide surface layer formed on the alloy 8090 after being solution heat treated in air at 803 K, and also found that surface depletion of Li resulted in softening to depths of up to 0.5 mm. Burke and Papazian [6] performed thermogravimetric analysis on a series of Al–Li alloys and found

that (a) the greater the Li content, the faster the oxidation, and (b) oxidation proceeded much faster in a moist air atmosphere than in dry air, an observation also made by Fields *et al* [7].

In the present research, positron annihilation has been used to study the effect of heat treatment and Li depletion on Al–Li alloys. Stott and Kubica [8] predicted theoretically a strong affinity between positrons and Li atoms in an Al matrix. del Rio *et al* [9] demonstrated this experimentally, and del Rio and de Diego [10] have shown that if the Li is depleted to a level below a critical concentration of 0.5 at.% the trapping of positrons by Li atoms is markedly reduced. Consequently, at low Li concentrations, positron trapping is primarily by open-volume defects.

Fretwell *et al* [11] observed Doppler broadening of the positron annihilation linewidth to study the effect of cold working and quenching on pure Al and Al with 1.9 and 12 at.% Li. When the three specimens were quenched from elevated temperatures after annealing in an argon atmosphere a substantial increase in the lineshape parameter S [12] was observed, due to the presence of open-volume defects in much greater concentrations than in well annealed pure Al. On ramp heating the quenched alloy with 12 at.% Li the S parameter exhibited an upward trend; S for the other two samples exhibited prominent peaks centred at about 260 K, attributed to vacancy cluster formation and collapse.

2. Theoretical considerations

McAlister [2] has developed an empirical expression for the solubility limit for Li in Al by fitting experimental data for several alloys:

$$\ln(X_{Li}) = -0.2708 - 1496.8/T \quad (1)$$

where X_{Li} is the saturation atomic fraction of Li in the Al solid solution and T is the absolute temperature. (The phase diagram by McAlister was used in this research in preference to some of those reviewed by Williams [13] because we are primarily concerned with solid solutions.) The saturation limit temperatures calculated from (1) for the alloys used in the present experiment are given in table 1. Note that these temperatures are all below the ambient temperature. Also shown in table 1 are the vacancy concentrations at 873 K, c_v , calculated using the expression developed by Lomer [14]:

$$c_v = \exp(S_f/k)[(1 - 12c_{Li}) \exp(-E_f/kT) + 12c_{Li} \exp(-(E_f - E_B)/kT)] \quad (2)$$

where c_{Li} is the atomic fraction of Li and 12 is here the co-ordination number of the lattice. The value of the vacancy formation enthalpy H_f ($\approx E_f$, the vacancy formation energy) has been determined to be 0.66 eV using positron spectrometry [15]. The Li–vacancy binding energy is found to be 0.26 eV from the empirical expression developed by Doyama and Cotterill [16]. Finally, $S_f/k = 2.4$, where S_f is the formation entropy [17]. Lomer's expression assumes that the major contributions to E_B are from the nearest neighbour shell; equation (2) is valid for low Li concentrations for which the formation of vacancy complexes with more than one Li atom is unlikely, and it is assumed that this is the case in the present study.

3. Experimental considerations

Heating Al–Li alloys in either very dry air or very dry, very pure nitrogen at 873 K may allow some reaction between the alloy surface and the atmosphere to occur. In the latter case a very small amount of reaction products forms on the surface, as determined by

thermogravimetric measurements of Averill *et al* [18]; they probably observed the formation of a small amount of AlN, whose free energy of formation is much more negative than that for Li₃N [19–21]. In contrast, when heating these alloys in very dry air Li₂O is formed on the surface [22] because its free energy of formation is more negative than for Al₂O₃ [17–19].

Therefore, whereas annealing in very dry, very pure nitrogen at 873 K will introduce a negligible number of vacancies in excess of the equilibrium concentration as calculated by equation (2), oxidation in dry air will cause preferential depletion of Li beneath the surface, introducing excess vacancies into the bulk by the Kirkendall effect [4]. One can assume that the steady-state concentration of excess vacancies will be some function of Li concentration.

After severe quenching, it has usually been assumed that most of the vacancies existing at the annealing temperature are retained as monovacancies within the alloy crystal lattice, or perhaps as very small vacancy clusters, divacancies etc. Guyot [23] has shown that screw dislocations will capture vacancies during quenching to form helical dislocations; this causes a reduction in the number of vacancies available for trapping positrons. We shall return to this effect later.

4. Experimental procedure

A series of Al–Li alloys were prepared from high-purity Al and Li, with Li contents of 230, 660, 1240, 1870 and 2760 ppm (as determined by chemical analysis of the cast alloys). These Li contents were low enough to make certain that essentially Al–Li solid solutions were being studied throughout most of the temperature range of this experiment, and are lower than the critical concentrations for Li–positron binding observed by del Rio and de Diego [10]. After the alloys were melted and cast into cylindrical ingots they were rolled into plates of thickness ~ 6 mm. Because of possible loss of Li by oxidation or evaporation during processing, both surfaces of each plate were then milled—reducing the final plate thicknesses to 1.5 mm. Disc specimens 9 mm in diameter were punched from the milled plate.

To heat treat the specimens pairs of discs of the same alloy were suspended together on a thin Mo wire within a stainless steel shroud positioned near the control thermocouple in a vertical tube annealing furnace. During heat treatment at 873 K for 1 h the flow of gas—either very dry air or very dry, very pure N₂—was regulated to ensure a change of atmosphere in the tube furnace every 90 s. The gas train used to dry and purify the two gases was similar to that described by Alam *et al* [12], except that the source of the gases was a high-pressure gas cylinder rather than a mechanical air pump. To reduce the residual O₂ in the high-purity N₂ to a level below 20 ppm, the N₂ was passed over Cu turnings at 773 K.

After annealing the specimens were dropped into concentrated HCl at 160 K. After cooling to this temperature the specimens were cooled further in liquid N₂ and then assembled with a ²²Na source in a small stainless steel box. The box was then mounted in the heater stage of a liquid N₂ cold finger assembly and encased in a vacuum chamber evacuated to 1.3×10^{-4} Pa. The specimens were then gradually heated from ~ 90 K at a rate of about 8 K h⁻¹. The energy spectra of the annihilation photons were measured by a Ge detector–multichannel analyser system. $\sim 10^6$ counts were recorded in about 1200 s in the photopeak, from which one obtains the *S* parameter, which describes the Doppler-broadened linewidth [24].

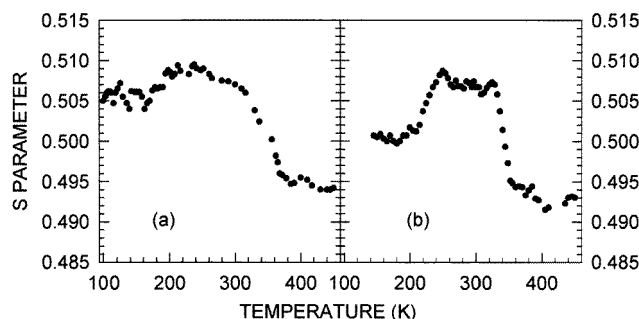


Figure 1. (a) S parameter against temperature for Al-660 ppm Li alloy annealed in very dry air. (b) S parameter against temperature for Al-1870 ppm Li alloy annealed in very dry, very pure nitrogen.

5. Results and discussion

Representative S - T plots for the alloys annealed in dry air and in dry nitrogen are shown in figures 1(a) and (b), respectively (data for all samples in the two sets are similar to those shown). Each exhibits a broad peak associated with vacancy clustering, whose onset and end temperatures (150 and 360 K for samples annealed in air, and 190 and 360 K for nitrogen, all ± 10 K) are essentially independent of Li content. The peak ‘height’, $\Delta S \approx 0.01$, is similar to that assigned by Fretwell *et al* [11] to the formation of vacancy clusters; they observed an onset temperature close to the 190 K reported here for the samples annealed in nitrogen.

As discussed in section 3 annealing in very pure, very dry nitrogen creates a negligible number of excess vacancies via evaporation of Li from the surface and limited surface oxidation, in contrast to the situation for alloys annealed in dry air. The observed difference between the vacancy clustering onset temperatures between the two sets of samples studied in the present experiment can be attributed to the formation of divacancies in the case of the air-annealed samples. Assuming that the probabilities of vacancy and divacancy migration are proportional to $\exp(-E_{1v}^m/kT)$ and $\exp(-E_{2v}^m/kT)$, where E_{1v}^m and E_{2v}^m are the vacancy and divacancy migration energies, respectively, then the ratio of clustering onset temperatures in the air- and nitrogen-annealed samples should be in the ratio E_{2v}^m/E_{1v}^m . Using $E_{1v}^m = 0.65$ eV and $E_{2v}^m = 0.48$ eV [25] this ratio is 0.74, in reasonable agreement with the observed ratio of 0.79 ± 0.07 . The divacancy model is supported also by the somewhat higher initial value of the S parameter in the air-annealed samples (see figure 1(a)); S increases with defect size to an asymptotic limit characteristic of large clusters or voids.

Li-vacancy binding would lead to a relative impediment to vacancy migration (and thus clustering) in the nitrogen-annealed samples, in which there is a significantly higher Li:vacancy ratio. However, as the clustering onset temperature in these samples is similar to that seen in earlier work on pure Al [11], this effect is assumed to be small compared with that of divacancy formation discussed in the previous paragraph.

The independence of the results on Li content implies that there are enough vacancies in the quenched samples to enable saturation positron trapping. This is supported by the concentrations c_v presented in table 1.

During quenching helical dislocations are generated by the capture of supersaturated vacancies by screw dislocations [23]. From the S - T plots it appears that for most of the

Table 1. The saturation limit temperature and vacancy concentration c_v at 873 K as a function of Li content in Al–Li alloys.

Li atomic fraction (ppm)	Saturation temperature (K)	c_v at 873 K (10^{-3} per atom) [14]
0	—	1.701
230	185	1.846
660	212	2.115
1240	233	2.479
1870	249	2.875
2760	266	3.433

Al–Li alloys annealed in dry air or nitrogen there are more than enough vacancies to supply the growth in the helical dislocations and to retain enough trapped vacancies to provide for the vacancy clustering.

6. Summary

Doppler broadening spectroscopy of severely quenched Al–Li solid solution alloys has demonstrated that the onset temperature for vacancy clustering in samples annealed initially in dry air is 40 ± 15 K lower than that in very dry, very pure nitrogen. This difference may be understood in terms of the lower Li concentration and correspondingly higher vacancy concentration in the air-annealed samples as a result of preferential migration of Li to, and oxidation at, the surface. In the oxygen-annealed samples the substantially higher vacancy concentration leads to the formation of divacancies, which migrate at a lower temperature consistent with a simple model employing migration energies for vacancies and divacancies in Al. The measured onset temperature of 190 ± 10 K for the nitrogen-annealed samples is consistent with the value observed by Fretwell *et al* [11] for pure Al. Retardation of vacancy migration by Li–vacancy binding may add further to the observed difference between the results, but its effect is considered to be small. No significant effect of Li concentration was seen in any of the data sets, indicating saturation in the positron response to vacancy-type defects in each case.

Acknowledgments

The authors wish to thank F Gayle, formerly with Reynolds Metals and now of NIST, for providing the Al–Li alloys and their chemical analysis. The authors also wish to thank the ever-helpful technicians in the School of Physics, University of East Anglia. One of the authors (HPL) wishes to thank the School of Physics for the opportunity to perform this research using their facilities.

References

- [1] Wang W and Grant N J 1983 *Aluminium–Lithium Alloys II* ed E A Starke *et al* (Monterey, CA: Metallurgical Society) p 466
- [2] McAlister A J 1982 *Bull. Alloy Phase Diagram* **3** 177
McAlister A J 1984 *Bull. Alloy Phase Diagram* **5** 21
- [3] Papazian J M, Schulte R L and Adler P N 1986 *Metall. Trans. A* **17** 635
- [4] Smigelskas A D and Kirkendall E O 1947 *Trans. AIME* **171** 130
- [5] Holdway P and Bowen A W 1989 *J. Mater. Sci.* **24** 3841

- [6] Burke M and Papazian J M 1986 *Aluminium–Lithium Alloys III* ed C Baker *et al* (Oxford: Institute of Metals) p 287
- [7] Fields D J, Butler E P and Scamans G M 1980 *Aluminium–Lithium Alloys* ed T H Sanders Jr *et al* (Stone Mountain, GA: Metallurgical Society) p 325
- [8] Stott M J and Kubica P 1975 *Phys. Rev. B* **11** 1
- [9] del Rio J, de Diego N and Fink D 1989 *J. Phys.: Condens. Matter* **1** 4441
- [10] del Rio J and de Diego N 1991 *Phys. Status Solidi* a **124** K141
- [11] Fretwell H M, Duffy J A, Alam M A, Leighly H P Jr and Walmsley J 1995 *J. Phys.: Condens. Matter* **7** 4573
- [12] Alam M A, Leighly H P Jr and West R N 1982 *J. Phys. F: Met. Phys.* **12** 399
- [13] Williams D B 1989 *Aluminium–Lithium Alloys V* ed T H Sanders and E A Starke Jr (Birmingham: Materials and Component Engineering) p 551
- [14] Lomer W M 1958 *Vacancies and Other Point Defects in Metals (Inst. Metall. Monogr. Ser. 23)* (London: Institute of Metals) p 79
- [15] Triftshäuser W 1975 *Phys. Rev. B* **12** 4634
- [16] Doyama M and Cotterill R M J 1966 *Phys. Lett.* **23** 58
- [17] Dorn J E and Mitchell J B 1966 *Acta Metall.* **14** 71
- [18] Averill W A, Olson D L, Matlock D K and Edwards G R 1980 *Aluminium–Lithium Alloys* ed T H Sanders Jr *et al* (Stone Mountain, GA: Metallurgical Society) p 15
- [19] Kubaschewski O, Evans E L and Alcock C B 1967 *Metallurgical Thermochemistry* (London: Pergamon)
- [20] Popovich V 1967 *Mater. Sci.* **3** 17
- [21] Rosenquist T 1974 *Principles of Extractive Metallurgy* (New York: McGraw-Hill) p 514
- [22] Ashton R F, Thompson D S, Starke E A Jr and Lin F S 1986 *Aluminium–Lithium Alloys III* ed C Baker *et al* (Oxford: Institute of Metals) p 68
- [23] Guyot P 1971 *Phys. Status Solidi* a **5** 95
- [24] West R N 1979 *Positrons in Solids* ed P Hautojärvi (New York: Springer) p 89
- [25] Schüle W and Scholz R 1982 *Point Defects and Defect Interactions in Metals* ed J-I Takamura, M Doyama and M Kiritani (Tokyo: Tokyo University Press) p 257