



THERMAL EXTRACTION OF Pb FROM THE BULK TO THE SURFACE IN Al DOPED WITH Pb

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Introduction

According to most recent data the solubility of Pb in Al is extremely small (1). In a systematic investigation into the influence of material purity and specific impurities on grain boundary motion we found (2-4) that an addition of 20 ppm Pb to pure Al drastically affects grain boundary mobility. The temperature dependence of grain boundary mobility in Al-20ppmPb revealed that there is a temperature, at which both the migration activation enthalpy and preexponential mobility factor rise steeply. We interpret this result as a wetting phase transition in the grain boundary and attribute the unstable motion of grain boundaries in the low temperature regime to a boundary motion dragged by small drops of liquid lead (3). On this basis, the temperature dependence of grain boundary mobility proves that even at concentrations as low as 20 ppm Pb is not soluble in Al, but contained as small inclusions (particles) which are liquid at temperatures higher than the melting point of Pb. This causes interesting phenomena and side effects, when such a material is subjected to a heating cycle as will be reported and discussed in this paper.

Experimental Procedure and Results

The experiments were carried out on bicrystals of pure Al (99.999at%) alloyed with 20ppmPb. The alloy was prepared under industrial conditions using induction stirring. The concentration of Pb in the prepared alloy was determined by glow discharge mass-spectrometry.

The bicrystals were grown by directional crystallization with the cooling seed in a horizontal mold. Samples with $40^\circ\langle 111 \rangle$ tilt grain boundaries were prepared. Their dimensions were 8 mm width, 15 mm length and 2 mm thickness.

The experiments were conducted in the following manner: The sample was mounted onto a hot stage of an optical microscope. At first the sample was heated up to 300°C, kept at this temperature for 3 minutes and slowly cooled down. During the cooling phase a grain boundary groove emerged on the crystal surface. Then the sample was heated up to a relatively high temperature (600°C), held at this

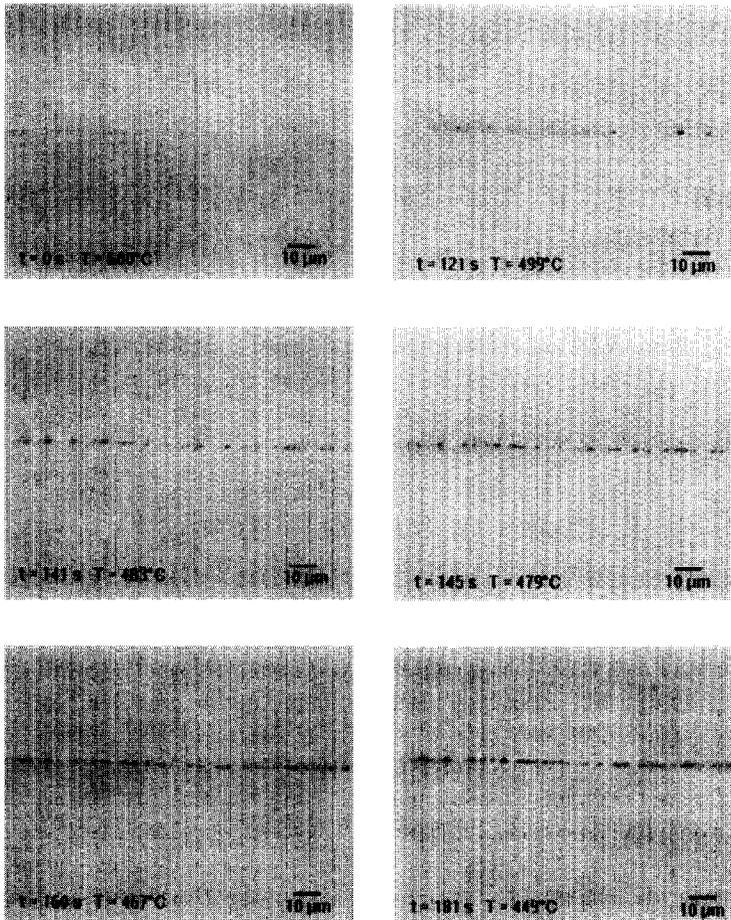


Figure 1. Select video frames of the bicrystal during the cooling from 600°C at a rate of 50°/min.

temperature for 3 minutes and cooled down at a constant rate (50°/min). The sample surface in the vicinity of the grain boundary groove was constantly monitored through an optical microscope and recorded on a video tape. A select sequence of video frames is given in Fig. 1. After 110-130 s from the beginning of a cooling cycle individual lense-shaped particles appeared in the boundary groove. The drops grew quickly and reached a size up to 5 μm within 70-90 s. After 30-40 s subsequent to the appearance of the first drops, also round drops were observed on the crystal surface outside of the boundary groove. Fig. 2 shows the bicrystal surface at higher magnification in a SEM after cooling to room temperature.

For a qualitative analysis of the observed effect the sample was cooled down until the first lead drops appeared on its surface, then the temperature was kept constant till the drops reached a steady state (Fig. 3).

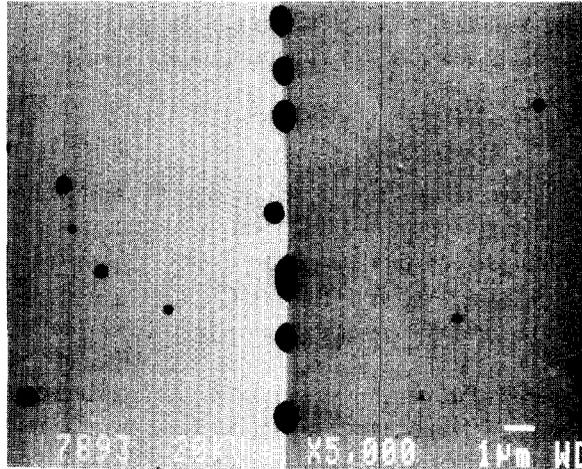


Figure 2. SEM image of bicrystal surface after the complete heating/cooling cycles.

Discussion

Concept

Obviously, during cooling of the Al-20ppmPb alloy, Pb is extracted from the bulk to the surface, primarily at the intersection of grain boundary and free surface. We propose the following interpretation of the observed phenomenon. The lead atoms are bonded to excess vacancies, which leave the crystal

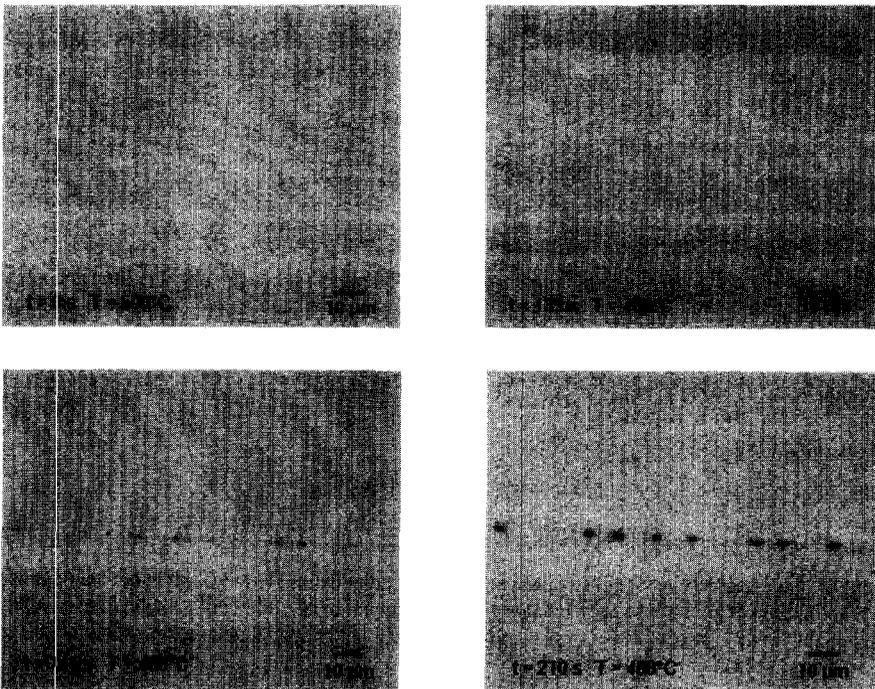


Figure 3. Video frames of the bicrystal during the cooling from 600°C to 488°C.

via the grain boundary during cooling in order to establish the thermal equilibrium. In the following we will show that this interpretation is in qualitative and quantitative agreement with experimental results.

Vacancy Concentrations

An important characteristic of vacancies is that there is no law of conservation for vacancies (in contrast to atoms), i.e. vacancies may appear and disappear. With increasing temperature the vacancy concentration N_v rises according to equation $N_v = \exp(-G_v^f/kT)$ (G_v^f is the Gibbs free energy of vacancy formation), i.e. new vacancies have to be formed. Conversely, with decreasing temperature the vacancy concentration decreases, therefore, vacancies have to leave the crystal. In case of a substantial oversaturation the main sink for vacancies is the free surface, which is a vacancy sink of infinite strength. Vacancies move by diffusion, which proceeds fastest along dislocations and grain boundaries. As a result of the excess vacancy diffusion along dislocations and grain boundaries to the free surface, grooves and pits are formed at locations where grain boundaries and dislocations intersect the surface¹.

In real crystals besides free vacancies also vacancy-defect complexes may be formed, among which vacancy (v)-impurity atom (p) pairs have a special significance. The physical reason for the formation of such pairs is the lattice relaxation in the vicinity of an impurity atom by the attachment of a vacancy. The total concentration of vacancies in thermal equilibrium is the sum of free vacancies (N_{vo}) and vacancies attached to impurity atoms (N_{vp}). Lomer (5) derived the concentration of "vacancy-impurity atom" pairs from a simple model. If Z is a number of next neighbours, and if there are N_p impurity atoms

$$N_{vp} = zN_p \exp\left[-(G_v^f - \Delta G_{vp})/kT\right], \quad (1)$$

where G_v^f is the free energy of vacancy formation in the pure solvent and ΔG_{vp} is the impurity atom-vacancy interaction free energy. Introducing the interaction energy ϵ , i.e. $\Delta G_{vp} = -(\epsilon + pV) - TS_{vp}$, eq. (1) reads (6)

$$N_{vp} \cong zN_{vo}N_p \exp(\epsilon/kT) \quad (2)$$

where $N_{vo} = \exp(-G_v^f/kT)$ is the vacancy concentration in a pure solvent.

We propose to attribute the appearance and growth of lead drops on the surface to the exit of "vacancy-impurity atom" complexes along grain boundaries (and dislocations) to the free surface.² To prove this, let us consider what happens to the grain boundary, when the temperature is decreased from T_1 to T_2 . At temperature T the concentration of "vacancy-impurity atom" pairs (VIP) in the grain boundary N_{vp}^b is given in analogy to Eq. (2)

$$N_{vp}^b = zN_{vo}^b N_p^b \exp(\epsilon/kT), \quad (3)$$

¹In investigations of grain boundary motion the boundary position is often determined from grain boundary grooves, which are created by the condensation of excess vacancies along a grain boundary at the surface during cooling of a sample (7, 8). (Such groove may be called "vacancy groove" rather than a groove by "thermal etching"). Therefore, investigations of grain boundary motion must not be conducted on preheated and cooled specimens.

²In the following we will consider only the process of lead extraction along the grain boundary, though there are other defects in the crystal (dislocations), and an exit of separate "vacancy-impurity atom" -pairs directly from the bulk of the crystal is also not prohibited. These ways of lead extraction may be neglected in a first approximation.

where N_p^b and N_{vo}^b are the concentrations of impurity and free vacancies in the grain boundary, respectively.

The difference between the concentration of free thermal vacancies in the boundary and in the bulk is due to the different energies of vacancy formation. Let us define the free energy of vacancy formation in the boundary by $G_v^f - \sigma^*$, where σ^* is the boundary free energy per atom, then

$$N_{vp}^b = zN_p^b \exp\left(-\frac{H_v^f - \sigma^*}{kT}\right) \exp\left(\frac{\varepsilon}{kT}\right) = zN_p^b N_{vo} \exp\left(\frac{\sigma^*}{kT}\right) \exp\left(\frac{\varepsilon}{kT}\right) \quad (4)$$

With decreasing temperature the concentration of VIP in the boundary has to decrease. An excess of VIP together with an excess of free boundary vacancies will exit along the boundary to the free surface. But at the same time a flux of excess bulk vacancies, defined by the difference between vacancy concentrations in the bulk at temperatures T_1 and T_2 , is directed toward the boundary. The concentration of free and impurity bonded vacancies in the boundary will be higher than the equilibrium concentration as long as an excess of both types of vacancies has not left the boundary to the free surface and the equilibrium concentration of vacancies and VIP in the bulk (and in the boundary) is not yet established.

The Volume of Extracted Lead

The change of the VIP concentration in the boundary owing to a change of the free vacancy concentration in the bulk can be calculated under the assumption that at any moment the equilibrium between the vacancy concentration in the bulk and in the boundary is established. In particular, when all concentrations correspond to thermodynamic equilibrium, the change of VIP in the boundary upon cooling from T_1 to T_2 is equal to

$$\begin{aligned} \Delta N_{vp} = & zN_p^b(T_1)N_{vo}(T_1) \exp\left(\frac{\sigma^*}{kT_1}\right) \exp\left(\frac{\varepsilon}{kT_1}\right) - \\ & - zN_p^b(T_2)N_{vo}(T_2) \exp\left(\frac{\sigma^*}{kT_2}\right) \exp\left(\frac{\varepsilon}{kT_2}\right) \end{aligned} \quad (5)$$

The volume of lead V_{pb} extracted to the surface is given by the number of vacancies leaving the bicrystal through the grain boundary and the volume of lead Ω_{pb} (i.e. the atomic volume of lead) carried by each vacancy. With a (volume) concentration change of ΔN_{vp} vacancies and the number of atom per unit volume $N = 1/\Omega_{Al}$, where Ω_{Al} is the atomic volume of Al,

$$V_{pb} = V_{eff} \cdot \Delta N_{vp} \cdot \frac{\Omega_{pb}}{\Omega_{Al}} \quad (6)$$

where V_{eff} is the volume that contributes to the vacancy flux to the surface through the grain boundary. Under the assumption that the equilibrium concentration in the boundary is always established, i.e. all surplus vacancies in the boundary take to the free surface, then $V_{eff} = d/2 \cdot \ell \cdot 2\delta$, where $\delta(t)$ is the diffusion length of the vacancies in the bulk, i.e. 2δ is the effective thickness of the layer adjacent to the boundary that contributes to the vacancy flux from the bulk to the grain boundary. It depends on time: $\delta \approx \sqrt{D_v \cdot t}$, where D_v is the vacancy diffusion coefficient in the bulk, but has an upper bound

TABLE 1
Results of Quantitative Estimation of "vacancy-lead atom" Interaction Energy in Al

Number of experiment t	Anneal temperature T_1 , °C	Lead extraction temperature T_2 , °C	Extracted lead volume V_{pb}/ℓ , m^3/mm	Interaction energy ϵ_{pb} , eV
1	600	488	$2.4 \cdot 10^{-15}$	0.28
2	600	492	$1.9 \cdot 10^{-15}$	0.26
3	600	492	$2.6 \cdot 10^{-15}$	0.29
4	600	492	$1.5 \cdot 10^{-15}$	0.26
5	600	477	$2.0 \cdot 10^{-15}$	0.26
6	600	477	$2.2 \cdot 10^{-15}$	0.27

$\delta_{max} = d/2$, since more remote vacancies will reach the free surface before entering the grain boundary. Also, it is tacitly assumed that the volume will provide the surplus vacancies, while the lead atoms are scavenged by the vacancies in the grain boundary.

In a series of experiments the extracted volume was measured after equilibrating the sample at 600°C with no lead on the surface, cooling to about $485 \pm 7^\circ\text{C}$ and holding at that temperature until the growth of the lead drops on the surface ceased (Table 1). There is a substantial scatter of the measured amount of extracted lead, which obscures any temperature dependence in the small final temperature interval. The scatter is mainly attributed to the poor statistics of the small number of lead drops on the surface. The extracted lead volume per unit length $V_{pb}/\ell = (2.1 \pm 0.5) \cdot 10^{-15} m^3/mm$ can be used to determine the vacancy-lead interaction energy ϵ from eqs.(5)-(6).

$$V_{pb} = z N_p^b \left\{ N_{vo}(T_1) \exp\left(\frac{\sigma^* + \epsilon}{kT_1}\right) - N_{vo}(T_2) \exp\left(\frac{\sigma^* + \epsilon}{kT_2}\right) \right\} V_{eff} \cdot \frac{\Omega_{Pb}}{\Omega_{Al}} \quad (7)$$

Pair Interaction Energy and Boundary Structure

Using the observed amount of lead, the following literature data $D_{ov} = 1.7 \cdot 10^{-4} m^2/s$, $H_f^l = 0.81 eV$ (9), the specimen thickness $d = 2 \cdot 10^{-3} m$ and an estimate of $\sigma^* \cong 0.4 eV$ based on a boundary three atomic layers in width, we obtain³ $\epsilon = 0.27 \pm 0.01 eV$ under the assumption that the boundary consists completely of lead, i.e. $N_p^b = 1$. This assumption is justified from the following reasoning. Let us assume that all lead in the boundary would be extracted to the surface. Then the volume of the intergranular area V_{ig} would correspond to the extracted volume V_{pb} , $V_{ig} = \ell \cdot d \cdot \zeta = V_{pb}$, where ζ is the width of the interfacial volume. From the measurement of V_{pb} , the evaluated boundary length ℓ and the specimen thickness d , we obtain $\zeta \cong 4-6 nm$, corresponding to $\zeta > 10b$, b -atomic diameter, while grain boundaries are usually narrow and comprise at most 3 atomic spacings as evident from HREM observations or computer simulations. However, the estimate of $\zeta > 10b$ is only a lower bound, since not all lead will leave through the boundary during the imposed temperature drop. In fact, even for an alloy of Al with 20ppmPb we have to conclude that the boundary consists of a wide layer of lead and, therefore, above the wetting phase transition the boundary constitutes a layer of liquid lead. The value obtained for the pair interaction energy $\epsilon = 0.27 eV$ is in good agreement with literature data on vacancy-impurity

³ ϵ varies with V_{pb} only on a logarithmic scale. Therefore, it is hardly affected by the scatter of V_{pb} .

interaction energies. For example, for gold in aluminium $\epsilon_{Au} = 0.38$ eV, for indium $0.39 \leq \epsilon_{In} \leq 0.42$ eV, or for tin $0.42 \leq \epsilon_{Sn} \leq 0.46$ eV (9). It is noted, that the value $\epsilon = 0.27$ eV is a low estimate, since the volume of lead extracted to the free surface along dislocation lines was not taken into account, i.e. the concentration of vacancies leaving the crystal through the grain boundary is *overrated*.

Conclusions

1. The extraction of lead along grain boundaries during a temperature drop was observed in a Al20ppmPb alloy.
2. The observed phenomenon is interpreted in terms of thermal excess vacancies carrying lead atoms to the surface while leaving the bulk via grain boundaries (or dislocations).
3. From the measured amount of extracted lead it follows that the boundary is fully saturated with lead and essentially comprises a thick layer of lead.
4. The bonding energy of lead atoms to vacancies was derived to amount to $\epsilon \cong 0.27$ eV.

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