



ON THE EFFECT OF PURITY AND ORIENTATION ON GRAIN BOUNDARY MOTION

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Abstract—The influence of impurities on grain boundary mobility in a $\Sigma 7$ ($38.2^\circ < 111 >$) and in an off-coincidence boundary ($40.5^\circ < 111 >$) was investigated. The grain boundary mobility was found to strongly depend on grain boundary crystallography and material purity. The measured concentration dependence of activation enthalpy and preexponential mobility factor did not comply with predictions of traditional impurity drag theory. An extended impurity drag theory is presented that takes into account interaction of the adsorbed atoms in the boundary. This theory predicts a concentration dependence of the activation enthalpy. For the $\Sigma 7$ boundary it can explain qualitatively the frequently observed high values of preexponential mobility factor and activation enthalpy. The compensation temperature was found to depend on composition. © 1998 Acta Metallurgica Inc.

1. INTRODUCTION

It is well known that the purity of a material has a great influence on grain boundary motion. Impurity atoms almost always reduce the rate of grain boundary migration. However, very little is known on how solute atoms affect grain boundary motion besides the exerted drag, in particular, how impurities influence and thus interact with the grain boundary structure. Our current understanding of the orientation dependence of grain boundary mobility and the effect of solutes on this dependence is mainly founded in the classical work of Aust and Rutter, who investigated grain boundary migration in bicrystals of Pb [1–3], and also in results obtained by Shvindlerman and co-workers [4, 5] on bicrystals of Al and Zn. According to these results the orientation dependence of grain boundary mobility is a segregation effect: strongly ordered boundaries, i.e. low Σ coincidence boundaries segregate less and, therefore, move faster than random boundaries.

Recent theories of grain boundary motion in systems with impurities assume that the impurities follow the boundary by volume diffusion and, as a result, the activation enthalpy for migration is independent of impurity concentration. Less attention is paid to the mobility preexponential factor although, as it was shown recently [7], it is of equal significance due to the so-called compensation effect: a change of the activation enthalpy always causes a change of the preexponential factor such that the

effect of the changing activation enthalpy on migration rate is substantially mitigated.

In a previous paper [7] we reported on the temperature dependence of grain boundary mobility of $< 111 >$ tilt grain boundaries in the vicinity of the $\Sigma 7$ misorientation in high purity Al (Al I in Tables 1 and 2). The important result of the study was the finding that not only the activation enthalpy of migration increased with increasing deviation from the coincidence misorientation, but also the preexponential mobility factor rose drastically. However, it remains unclear, how impurities affect activation enthalpy and preexponential factor of grain boundary mobility of grain boundaries with different structure. This problem was addressed in the current study.

2. EXPERIMENTAL

The motion of pure $< 111 >$ tilt boundaries with misorientation angles in the vicinity of the special misorientation $\Sigma 7$ ($38.2^\circ < 111 >$) was studied (Table 2). The experiments were carried out on bicrystals produced from high purity aluminium of different production from Volhov's Aluminium Plant, Russia, 99.999% (hereafter referred to as Al I), Vereinigte Aluminium Werke, Germany, 99.9999% (Al II) and 99.9995% (Al V), Pechiney, France, 99.999% (Al III) and Sumitomo, Japan, 99.999% (Al IV).

For measurement of grain boundary mobility, the motion of grain boundaries under the action of a constant driving force was recorded (Fig. 1). The driving force p was provided by the surface tension σ of a curved grain boundary: $p = \sigma/a$, where a is

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Table 1. Concentration of impurities in differently pure Al (in ppb)

| Element | Aluminium | | | | |
|--------------------|-----------|-----|-----|------|------|
| | I | II | III | IV | V |
| Ag | — | — | — | — | — |
| As | — | 8 | — | — | 136 |
| B | — | — | 36 | 115 | 180 |
| Ba | — | — | — | 9 | 10 |
| Be | — | — | — | — | — |
| Bi | — | — | — | — | 52 |
| Cu | — | — | — | — | — |
| Ce | — | 12 | — | 515 | 988 |
| Cl | — | — | — | — | — |
| Co | — | — | — | — | — |
| Cr | 18 | — | 298 | 42 | 15 |
| Cs | — | — | — | — | — |
| Cu | — | — | 517 | — | 403 |
| F | — | — | — | — | — |
| Fe | 46 | 275 | 380 | 217 | 357 |
| Ga | — | — | 57 | — | — |
| Ge | — | — | — | — | — |
| In | — | — | — | — | — |
| K | — | — | — | — | — |
| La | — | — | — | 199 | 244 |
| Li | — | — | — | — | — |
| Mg | 212 | 92 | 299 | 985 | 71 |
| Mn | 43 | — | 105 | 10 | — |
| Mo | — | — | 17 | — | — |
| Na | — | 14 | — | 40 | 31 |
| Ni | — | — | 263 | 275 | 15 |
| O | — | — | — | — | — |
| P | — | 102 | 7 | 256 | 3740 |
| Pb | — | — | — | — | — |
| Pd | — | — | — | — | — |
| Pt | — | — | — | — | — |
| S | — | — | — | — | — |
| Sb | — | — | — | — | 43 |
| Si | 23 | 490 | 671 | 1910 | 992 |
| Sn | — | — | — | — | — |
| Ti | 65 | 17 | 354 | 198 | 123 |
| Th | — | 1 | — | 34 | 127 |
| U | — | — | — | 21 | 6.2 |
| V | — | 6 | 121 | 82 | 114 |
| W | — | — | — | — | — |
| Zn | — | — | 389 | — | 58 |
| Zr | — | — | 41 | — | 14 |
| Total content, ppm | 0.4 | 1.0 | 3.6 | 4.9 | 7.7 |

the width of the shrinking grain. Details of bicrystal growth and sample preparation are given elsewhere [7, 8]. The velocity of grain boundary motion was measured with an accuracy better than 2% [9] by using a specially designed X-ray device

for continuous tracking of a moving grain boundary (XICTD). The method of operation is illustrated in Fig. 1. A sample, which contains two differently oriented crystals is mounted under the incident X-ray beam such that one crystal is in Bragg-position, while the other is not. A scan of the X-ray beam along the sample surface would give the intensity distribution as shown in Fig. 1. The maximum intensity I_d is recorded as long as the X-ray spot is entirely located on the surface of crystal I. When the X-ray spot has completely moved over to crystal II the detected intensity attains the value I_0 . The boundary position can be associated with the position where an intermediate intensity $I_m = (I_0 + I_d)/2$ is detected. When the boundary moves, the sample is concurrently shifted such that the reflected X-ray intensity remains constant during the measurement. Thus, the velocity of the moving grain boundary is equal to the speed of sample movement at any moment during the experiment. Owing to the constant driving force, the investigated boundaries were observed to displace at a constant rate (Fig. 2). From the displacement versus time diagrams the velocity was determined.

The impurity concentration in the used materials was determined by glow discharge mass-spectrometry. The total impurity content in each material was defined as the sum of the concentration of all found elements (Table 1).

3. RESULTS

From the measured grain boundary velocity the reduced boundary mobility

$$A \equiv v \cdot a = A_0 \exp\left(-\frac{H}{kT}\right) = m\sigma, \quad (1)$$

was determined, where H is the activation enthalpy of migration A_0 a preexponential factor and m the grain boundary mobility. The latter is given by the ratio of velocity v and driving force p

$$m = \frac{v}{p} = \frac{v}{\sigma/a}. \quad (2)$$

Table 2. Misorientation and mobility parameters for the investigated $\langle 111 \rangle$ tilt grain boundaries in bicrystals of differently pure aluminium

| Misorientation angle (°) | Activation enthalpy (eV) | | | | | Pre-exponential factor (m^2/s) | | | | |
|--------------------------|--------------------------|-------|--------|-------|------|------------------------------------|------------------|------------------|------------------|------------------|
| | Al I | Al II | Al III | Al IV | Al V | Al I | Al II | Al III | Al IV | Al V |
| 37.1 | 1.69 | 1.89 | — | — | — | $2.0 \cdot 10^4$ | $1.9 \cdot 10^4$ | — | — | — |
| 37.4 | 1.32 | 1.64 | — | — | — | 31.6 | 446.7 | — | — | — |
| 37.7 | 1.28 | 1.53 | — | — | — | 25.1 | 80.8 | — | — | — |
| 37.9 | 1.23 | — | — | — | — | 20.0 | — | — | — | — |
| 38.2 ($\Sigma 7$) | 1.29 | 1.52 | 1.61 | 1.59 | 1.65 | 39.8 | 69.2 | 147.9 | 104.7 | 125.9 |
| 38.7 | 1.56 | 1.69 | — | — | — | $1.6 \cdot 10^3$ | 977 | — | — | — |
| 39.3 | 1.75 | 1.92 | — | — | — | $2.5 \cdot 10^3$ | $3.0 \cdot 10^4$ | — | — | — |
| 39.9 | 1.80 | 2.01 | — | — | — | $6.3 \cdot 10^3$ | $1.3 \cdot 10^5$ | — | — | — |
| 40.5 | 2.19 | 2.34 | 2.45 | 2.46 | 2.48 | $1.4 \cdot 10^5$ | $3.5 \cdot 10^7$ | $4.9 \cdot 10^7$ | $4.1 \cdot 10^7$ | $2.9 \cdot 10^7$ |
| 41.7 | 1.73 | 1.91 | — | — | — | $4.0 \cdot 10^4$ | $2.5 \cdot 10^4$ | — | — | — |
| 42.5 | 1.56 | — | — | — | — | $2.5 \cdot 10^3$ | — | — | — | — |
| 43.0 | 1.48 | 1.68 | — | — | — | 629.6 | 831.8 | — | — | — |

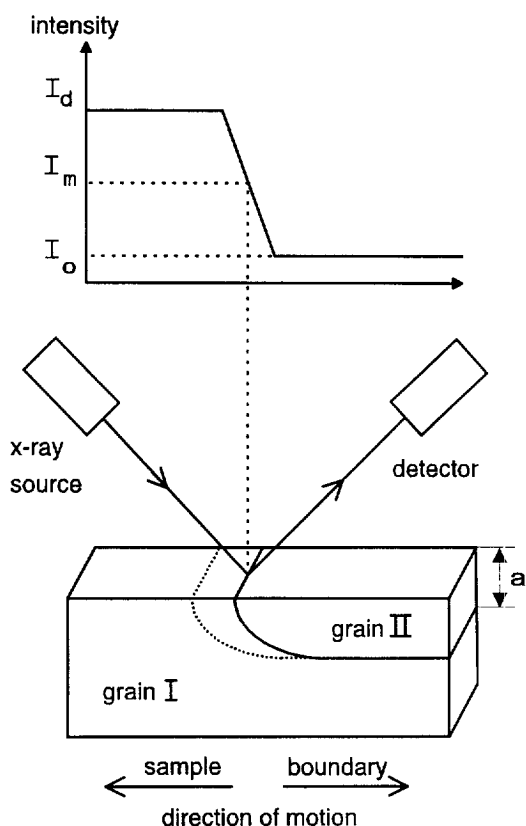


Fig. 1. Used bicrystal geometry for grain boundary motion measurements under a constant driving force, and measurement principle of the XICTD.

The reduced mobility* will be used in the following for sake of convenience. Figure 3 shows the temperature dependence of the reduced mobility for two 38.2° and 40.5° $\langle 111 \rangle$ tilt grain boundaries in samples of differently pure aluminium. These boundaries are of special interest because of their dominant role in recrystallization [7, 10]. In addition, the temperature dependence of grain boundary mobility for Al I and Al II was investigated in the angular interval of misorientation between 37° and 43° . The activation enthalpy was found to be constant for a given misorientation over the entire temperature range for each differently pure Al. The orientation dependence of boundary mobility in Al II showed the same qualitative temperature dependence as the purer Al I (Fig. 4). Above the "com-

*The reduced mobility is not a dimensionless quantity but the product of mobility and grain boundary surface tension. Therefore it reflects also the orientation and temperature dependence of grain boundary surface tension. However, according to computer simulations and measurements, the grain boundary surface tension may change by 20% or less but the reduced mobility may change by orders of magnitude. Therefore changes of the grain boundary surface tension can be neglected, if not absolute mobility values but activation parameters and mechanisms of grain boundary motion are considered, as in the case in the current paper

pensation temperature" $T_c = 430^\circ\text{C}$ the boundary with misorientation 40.5° had the highest mobility, while at lower temperatures the special boundary $\Sigma 7$ ($38.2^\circ \langle 111 \rangle$) moved with the highest mobility, as also found for Al I [7]. The dependence of the mobility of these two grain boundaries on solute content revealed a conspicuously large effect of impurity elements on boundary mobility (Fig. 5). An increase of the solute content from 0.4 to $7.7 \cdot 10^{-4}$ at.% decreased the boundary mobility by more than two orders of magnitude. In particular, the mobility of the off-coincidence $40.5^\circ \langle 111 \rangle$ boundary was more strongly affected by a rising impurity content than the mobility of the $\Sigma 7$ boundary. This became also apparent, when the orientation dependence of migration activation enthalpy was compared for two differently pure materials. Irrespective of solute content the minimum was attained for the $\Sigma 7$ boundary, while the boundary with 40.5° misorientation had a maximum activation enthalpy (Fig. 6, Table 2). With rising solute content the value of the activation enthalpy increased markedly for all boundaries, including coincidence ($\Sigma 7$) as well as off-coincidence boundaries (Fig. 7).

The preexponential mobility factor depended on misorientation angle φ in materials of different purity the same way as the activation enthalpy, i.e. a minimum of A_0 was obtained for the $\Sigma 7$ boundary, while the boundary with $\varphi = 40.5^\circ$ had the highest value of A_0 (Fig. 8, Table 2). But in strong

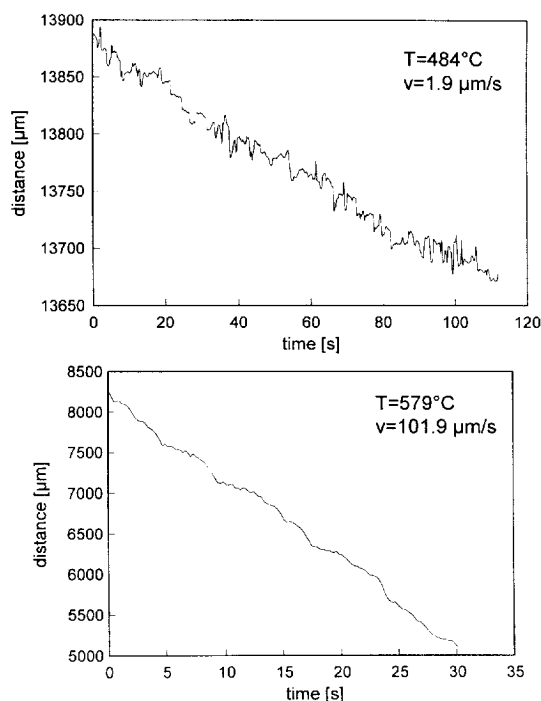


Fig. 2. Distance-time diagrams for $40.5^\circ \langle 111 \rangle$ tilt grain boundary migration at two different temperatures.

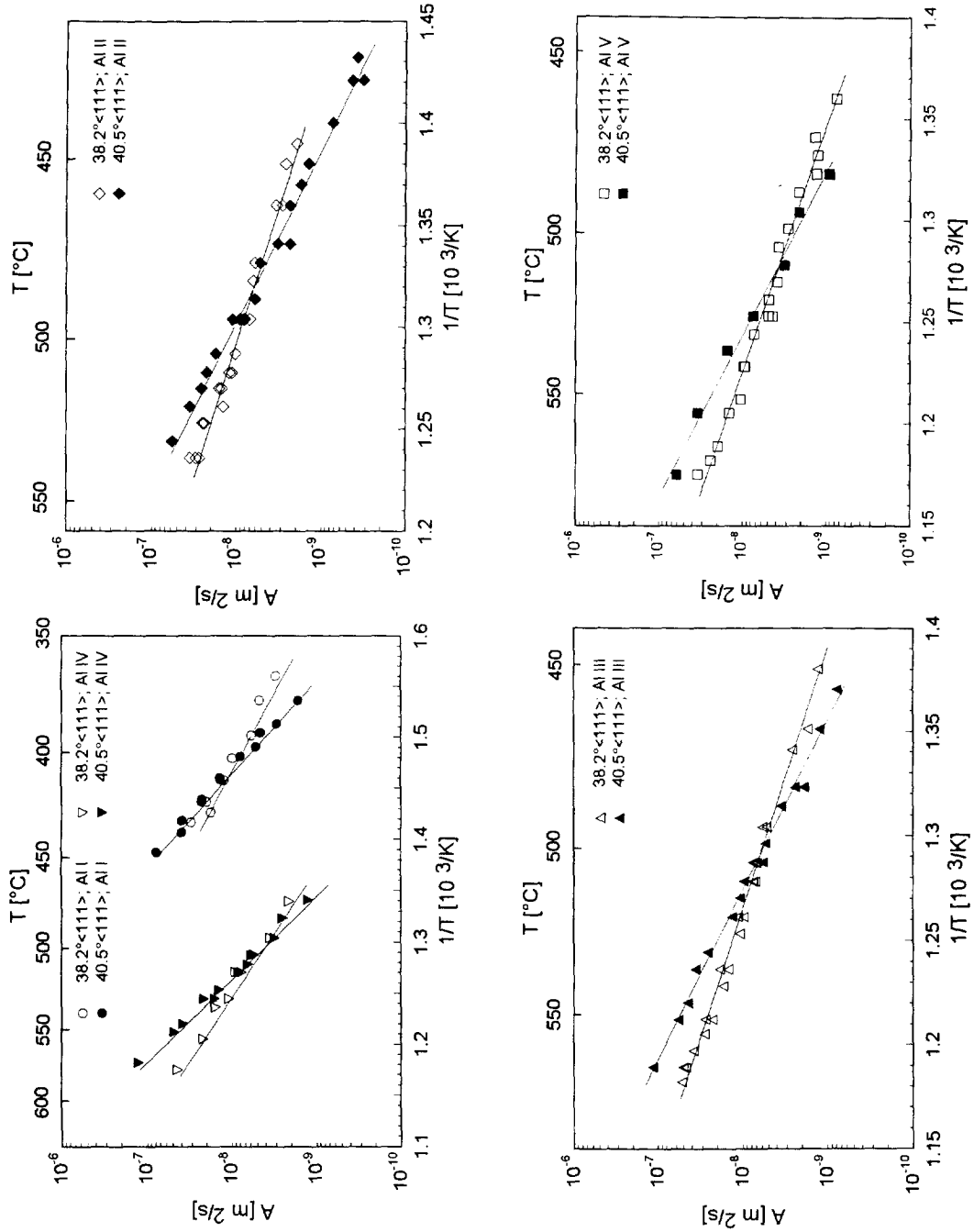


Fig. 3. Temperature dependence of the mobility A for 38.2 and 40.5° $\langle 111 \rangle$ tilt grain boundaries in differently pure aluminium.

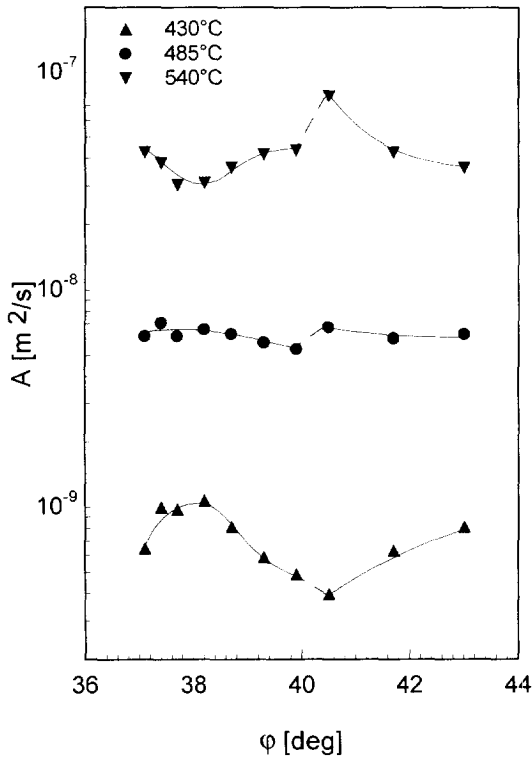


Fig. 4. Misorientation dependence of grain boundary mobility A for $\langle 111 \rangle$ tilt boundaries in Al II at different temperatures.

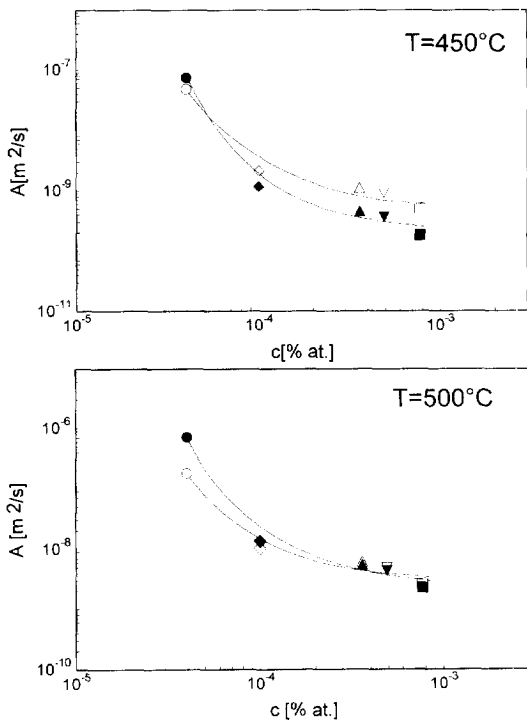


Fig. 5. Mobility A of 38.2° ($\Sigma 7$) (open symbols) and 40.5° (filled symbols) $\langle 111 \rangle$ tilt grain boundaries as a function of impurity concentration c in differently pure aluminium: \circ, \bullet —Al I; \diamond, \blacklozenge —Al II; $\triangle, \blacktriangle$ —Al III; $\nabla, \blacktriangledown$ —Al IV, \square, \blacksquare —Al V.

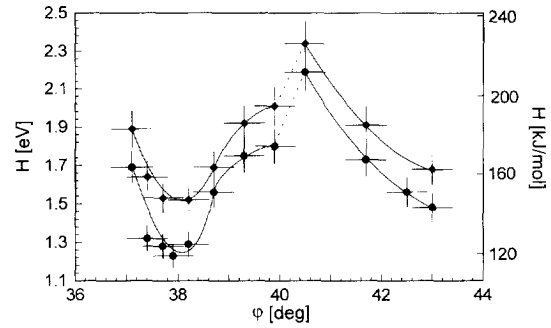


Fig. 6. Activation enthalpy H for migration of $\langle 111 \rangle$ tilt grain boundaries as a function of misorientation angle ϕ for two different aluminium charges: \circ —Al I; \blacklozenge —Al II.

contrast to the activation enthalpy, the value of the preexponential factor was practically independent of material purity (Fig. 9), unlike its dependence on misorientation angle (Fig. 8).

The change of activation enthalpy and mobility preexponential factor of the investigated boundaries in both materials (Al I, Al II) followed the compensation law, i.e. a linear relationship between H and $\ln A_0$ (Fig. 10). However, with increasing impurity content the compensation line H vs $\ln A_0$ was shifted towards larger values of activation enthalpy. As a consequence, also the compensation temperature was changed distinctly with rising solute content (Fig. 11).

4. DISCUSSION

4.1. Focus

In the following two major results of the current study will be given a more detailed consideration:

- (a) The mobility of the investigated grain boundaries depends strongly on material purity, because the activation enthalpy of grain boundary migration depends on impurity concen-

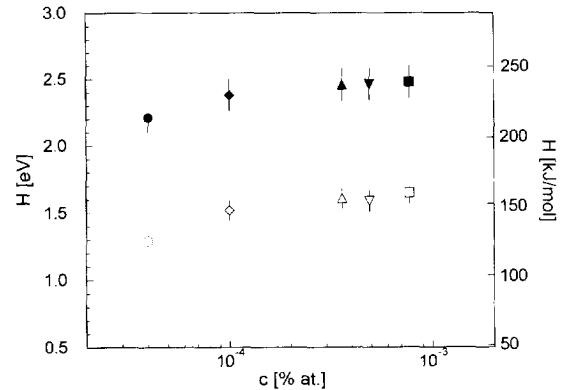


Fig. 7. The dependence of activation enthalpy H for migration of 38.2° (open symbols) and 40.5° (filled symbols) $\langle 111 \rangle$ tilt grain boundaries on impurity concentration c in differently pure aluminium: \circ, \bullet —Al I; \diamond, \blacklozenge —Al II; $\triangle, \blacktriangle$ —Al III; $\nabla, \blacktriangledown$ —Al IV, \square, \blacksquare —Al V.

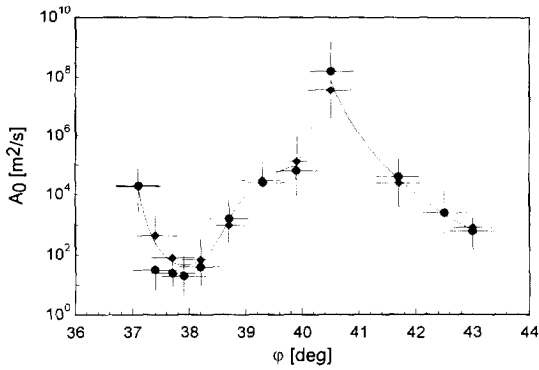


Fig. 8. Mobility preexponential factor A_0 of $\langle 111 \rangle$ tilt grain boundaries as a function of misorientation angle φ for two different aluminium charges: ●—Al I; ◆—Al II.

tration. With increasing impurity concentration the activation enthalpy rises for both coincidence and off-coincidence boundaries.

- (b) In contrast, the preexponential factor of the mobility equation is virtually independent of impurity content for a given misorientation, but irrespective of impurity level, it depends strongly on misorientation angle.

4.2. The relevant impurity concentration

As evident from Table 1, the total impurity concentration comprises a large number of elements, and since every element may interact differently with the grain boundary the question arises, which elemental concentration is to consider as most relevant for the overall migration behavior of the boundary. This problem is hard to address experimentally, since it is virtually impossible to produce theoretically pure binary alloys, thus probing one impurity element at a time. Also, there is no theoretical concept to date that adequately models the interaction of individual impurities with specific grain boundaries.

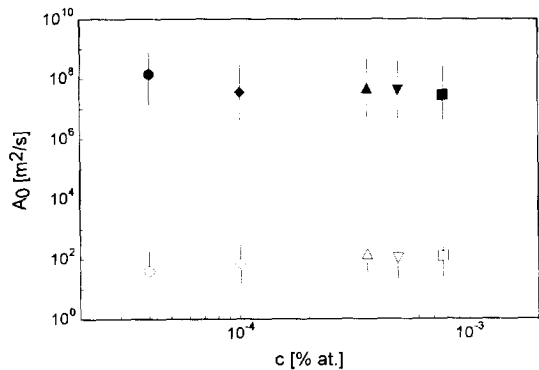


Fig. 9. The dependence of mobility preexponential factor A_0 of 38.2° (open symbols) and 40.5° (filled symbols) $\langle 111 \rangle$ tilt grain boundaries on impurity concentration c in differently pure aluminium: ○, ●—Al I; ◇, ◆—Al II; △, ▲—Al III, ▽, ▼—Al IV, □, ■—Al V.

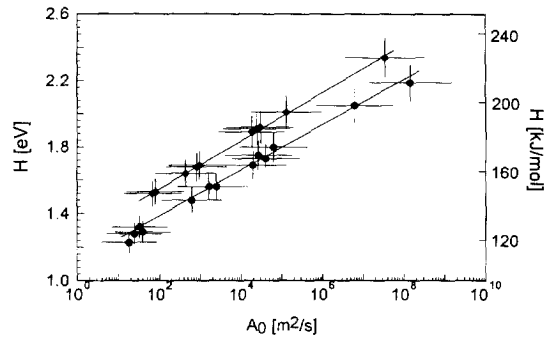


Fig. 10. The dependence of migration activation enthalpy H on preexponential mobility factor A_0 for the investigated $\langle 111 \rangle$ tilt grain boundaries in high purity aluminium of two different charges: ●—Al I; ◆—Al II.

We propose to consider the total impurity concentration as the relevant concentration for grain boundary migration because of the following reason. All materials used in the current investigation were high purity Al, which were produced by multiple pass zone refining. During zone melting only those impurities remain in the solid phase, which strongly interact with lattice defects, the structure of which is more akin to the liquid than to the crystalline state. Therefore, in a first approximation one may consider the residual impurities in pure materials to have high values of segregation energy, and we characterize the boundary-impurity interaction by a common enthalpy H_i and the total impurity concentration c .

4.3. Comparison with current impurity drag theories

The physical basis of grain boundary motion in a system with impurities was put forward by Lücke and Detert [11]. According to their theory, a boundary moves together with its segregated impurities. Correspondingly, the velocity of the impurity atoms v_{im} should be equal to the boundary velocity v_b , when the boundary moves under the action of an external driving force p . The grain boundary

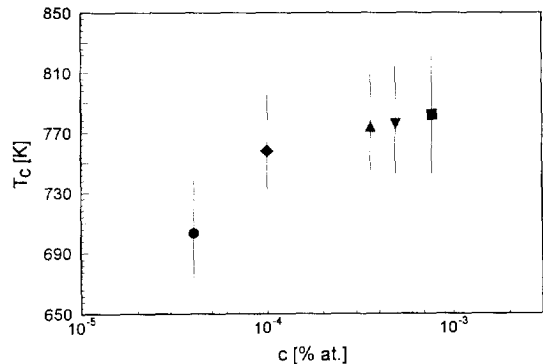


Fig. 11. The dependence of compensation temperature T_c on impurity concentration c in differently pure aluminium: ●—Al I; ◆—Al II; ▲—Al III; ▼—Al IV, ■—Al V.

imparts the same driving force to the carried along impurities.

$$v_b = m_b p = v_{im} = m_{im} \frac{p}{\Gamma}, \quad (3)$$

where m_b and m_{im} are the mobilities of boundary and impurity atoms, respectively. $\Gamma = c^b - c$ is the difference between the concentration of adsorbed impurities in the boundary c^b and the bulk concentration c . With the Nernst–Einstein relation

$$m_{im} = \frac{D}{kT}, \quad (4)$$

where D is the respective diffusion coefficient, equation (4) yields

$$m_b = \frac{m_{im}}{\Gamma} = \frac{D}{\Gamma \cdot kT}. \quad (5)$$

For dilute (volume) solutions Lücke and Detert used the Henry isotherm

$$\Gamma = N_a \cdot B \cdot c - c = c \left(N_a B_0 e^{\frac{H_i}{kT}} - 1 \right) \cong N_a B_0 e^{\frac{H_i}{kT}} \quad (6)$$

for $c << c^b$. ($B = e^{\frac{G_i}{kT}}$, $B_0 = e^{-\frac{S_i}{kT}}$, G_i —Gibbs free energy of adsorption, S_i —adsorption entropy, H_i —interaction enthalpy of impurity atoms with the boundary, N_a —number of adsorption sites in the boundary, c —volume impurity concentration.) equations (4)–(6) render the known expression for the mobility of a boundary with impurities:

$$m_b = \frac{D_0 e^{-\frac{(H_D + H_i)}{kT}}}{N_a B_0 kT \cdot c}, \quad (7)$$

where D_0 is the diffusion coefficient preexponential factor, H_D is the activation enthalpy for (volume) diffusion of the impurity atoms. According to equation (7) the activation enthalpy for grain boundary migration is the sum of two enthalpies, impurity diffusion and impurity adsorption.* The preexponential mobility factor changes inversely proportionally to the impurity concentration.† However, these conclusions are at variance with experimental results. As evident from Fig. 7, even at the lowest impurity content, the activation enthalpy

Broadly speaking, there is no reason to consider that the motion of impurity atoms on grain boundary during its movement happens by the mechanism of diffusion single transitions [7, 8, 12]. Therefore, impurity mobility should be written as $m_{im} = m_0 e^{-\frac{H_i}{kT}}$, where m_0 is a preexperimental factor, H^ is an activation enthalpy of impurity motion with grain boundary.

†The more sophisticated approaches of Cahn [12] and Lücke and Stüwe [13] have considered the behavior of impurity atoms near the moving boundary in more detail, but the here-derived conclusions remained unchanged.

‡It is pointed out that the partial areas as defined by equation (11) are, in general, not identical with the physical area fraction occupied by the respective elements in the boundary but are thermodynamical quantities exactly defined by this equation and may even assume negative values.

rises with increasing impurity concentration, whereas the preexponential factor remains essentially at the same level (Fig. 9).

4.4. Adsorption in grain boundaries

If there is a strong tendency toward segregation, the boundary impurity concentration may be high although the volume impurity concentration is small. For high impurity concentrations in the boundary it is necessary to take into account the mutual interaction of adsorbed atoms in the boundary. Also, as was shown experimentally [17], and theoretically [18], *grain boundaries are inhomogeneous*, i.e. not every site in the grain boundary is equally favourable for impurity segregation. The essential point here is that this inhomogeneity plays an important role for the adsorption during the process of migration [19] and thus, has to be taken into account.

The interaction between adsorbed atoms in the boundary has already been pointed out in the past [4, 15]. Recently, Lejcek and Adamek [16] took this interaction into account for modelling grain boundary migration by using the model of a regular solution. In particular, they showed that such an approach allows to explain the orientation dependence of migration activation enthalpy in systems with impurities.

In the following we shall consider the interaction of impurities with grain boundaries in terms of adsorption. This allows to express an influence of adsorption on both the activation enthalpy and the preexponential mobility factor. We consider a true binary system with bulk concentrations c_1 and c_2 and assume that the grain boundary chemistry is in equilibrium with the bulk in spite of GB motion.

$$\mu_1^b(\sigma, T, c_1^b) = \mu_1^v(p, T, c_1) \quad (8)$$

$$\mu_2^b(\sigma, T, c_2^b) = \mu_2^v(p, T, c_2) \quad (9)$$

where μ_1^b , μ_2^b and μ_1^v , μ_2^v are the chemical potentials of the first and second component in the bulk and in the boundary, respectively and c_1^b , c_2^b denote the respective boundary concentrations. The activities of atoms in both the bulk (a_1 , a_2) and the boundary (a_1^b , a_2^b) are related by [20]

$$\frac{a_1^b}{a_1} = \left(\frac{a_2^b}{a_2} \right)^{\frac{\sigma_1}{\sigma_2}} \cdot e^{-\frac{\omega_1(\sigma_2 - \sigma_1)}{kT}}, \quad (10)$$

where σ_1 and σ_2 are the grain boundary surface tensions of the pure first and second component, respectively, and

$$\omega_1 = - \left(\frac{\partial \mu_1^b}{\partial \sigma} \right)_{p, T} \Big|_{\sigma_1} \quad \text{and} \quad \omega_2 = - \left(\frac{\partial \mu_2^b}{\partial \sigma} \right)_{p, T} \Big|_{\sigma_2} \quad (11)$$

are the partial areas of the atoms of both components in the boundary.‡

Equation (10) constitutes the general adsorption isotherm, expressed in terms of activities. The relation between activity and chemical potentials of components in real and ideal solutions reads

$$a_i = c_i \exp\left(\frac{\mu_i - \mu_i^{\text{ideal}}}{kT}\right). \quad (12)$$

For consideration of the adsorption of impurities, which interact in the boundary and bulk solution, we can apply the Bragg-Williams approach for regular solutions, i.e. entropy changes are neglected.

With the known expressions for the enthalpy of components in a regular solution [21] the activity in such a solution can be represented as

$$a_1 = c_1 \exp\left(\frac{z\varepsilon \cdot (c_2)^2}{kT}\right), \quad a_2 = c_2 \exp\left(\frac{z\varepsilon \cdot (c_1)^2}{kT}\right), \quad (13)$$

where z is the coordination number, $\varepsilon = \varepsilon_{12} - \frac{1}{2}(\varepsilon_{11} + \varepsilon_{22})$ is the heat of mixing and ε_{ij} , ($i, j = 1, 2$) are the interaction enthalpies of the components.

Equations (10) and (13) yield for a regular solution in both bulk and boundary

$$\frac{c_1^b}{c_1} = \frac{\exp\left(\frac{z\varepsilon \cdot (c_2)^2}{kT}\right) \left[c_2^b \exp\left(\frac{z^b \varepsilon^b \cdot (c_1^b)^2}{kT}\right) \right]^{\frac{\omega_1}{\omega_2}}}{\exp\left(\frac{z^b \varepsilon^b \cdot (c_1^b)^2}{kT}\right) \left[c_2 \exp\left(\frac{z\varepsilon \cdot (c_1)^2}{kT}\right) \right]^{\frac{\omega_1}{\omega_2}}} \exp\left[\frac{\omega_1(\sigma_1 - \sigma_2)}{kT}\right] \quad (14)$$

where ε^b , z^b are the heat of mixing and the coordination number in the grain boundary.

Some special cases are of particular interest for an analysis of the experimental results of the current work.

- Both (bulk and boundary) solutions are regular, the heat of mixing and coordination number in both solutions are the same and the partial areas of the different species in the boundary are equal, i.e. $\varepsilon^b = \varepsilon$, $z^b = z$, $\omega_1 = \omega_2 = \omega$.

Then,

$$c_1^b = \frac{Bc_1 \exp\left[\frac{2z\varepsilon}{kT}(c_1^b - c_1)\right]}{1 - c_1 + Bc_1 \exp\left[\frac{2z\varepsilon}{kT}(c_1^b - c_1)\right]}, \quad (15)$$

where $B = e^{\frac{\omega(\sigma_2 - \sigma_1)}{kT}} = b_0 e^{\frac{H_i}{kT}}$, H_i —enthalpy of interaction between the boundary and an adsorbed impurity atom.

- The bulk solution is ideal, whereas the boundary solution is regular, i.e. $\varepsilon = 0$, $\varepsilon^b \neq 0$, $\omega_1 = \omega_2 = \omega$. In this case

$$c_1^b = \frac{Bc_1 \exp\left[\frac{z^b \varepsilon^b}{kT}(2c_1^b - 1)\right]}{1 - c_1 + Bc_1 \exp\left[\frac{z^b \varepsilon^b}{kT}(2c_1^b - 1)\right]} \quad (16)$$

For $c_1 < 1$, equation (16) is known as the Fowler-Guggenheim isotherm (1939).

- The same as case 2 but the partial areas of the species in the boundary are different, i.e. $\varepsilon = 0$, $\varepsilon^b \neq 0$, $\omega_1 \neq \omega_2$. In this case

$$c_1^b = c_1 \exp\left(-\frac{z^b \varepsilon^b \cdot (c_2^b)^2}{kT}\right) \cdot \exp\left[\frac{\omega_1(\sigma_2 - \sigma_1)}{kT}\right] \cdot \left\{ \frac{c_2^b}{c_2} \exp\left[\frac{z^b \varepsilon^b \cdot (c_1^b)^2}{kT}\right] \right\}^{\frac{\omega_1}{\omega_2}} \quad (17)$$

The condition closest to the current experiments is the case of an ideal bulk and a regular boundary solution. From equations (5) and (16) (denoting the impurity concentration as c and using the values for ε and z in the boundary)

$$m_b = \frac{m_{\text{im}}}{c^b - c} \cong \frac{m_{\text{im}}}{c^b} = \frac{m_0}{B_0 c}$$

$$\frac{\exp\left[-\frac{H^* + H_1 + \frac{z\varepsilon}{kT}(2c^b - 1)}{kT}\right]}{\left\{ 1 - c + Bc \exp\left[\frac{z\varepsilon}{kT}(2c^b - 1)\right] \right\}^{-1}} \quad (18)$$

For $\omega_1 \neq \omega_2$ equation (5) and (17) yield

$$m_b = \frac{m_{\text{im}}}{c^b - c} \cong \frac{m_{\text{im}}}{c^b} = \frac{m_0}{B_0 c}$$

$$\frac{\exp\left[-\frac{H^* + H_1 + (\beta - 1)z\varepsilon(1 - c^b)^2}{kT}\right]}{\left(\frac{1 - c^b}{1 - c}\right)^\beta} \quad (19)$$

with $\beta = \omega_2/\omega_1$. An important consequence of equations (18) and (19) is that the migration activation enthalpy includes the enthalpy of impurity motion involved in boundary migration, the adsorption energy (segregation of atoms in the pure boundary) and, in particular, the energy of interaction between adsorbed atoms. Therefore, the activation enthalpy of grain boundary migration becomes dependent on concentration, as indeed observed in experiment (Fig. 7).

Figures 12 and 13 show the dependence of boundary mobility and its parameters (A_0 , H) on impurity concentration for the investigated 38.2 and 40.5° <111> tilt grain boundaries as obtained by experiment and as calculated from equations (18) and (19), respectively. The calculations are in a good agreement with experiment at reasonable values of H^* , H_1 and $z\varepsilon$. (The magnitude of $B_0 = \exp(-S/k)$ changes in a very narrow range and

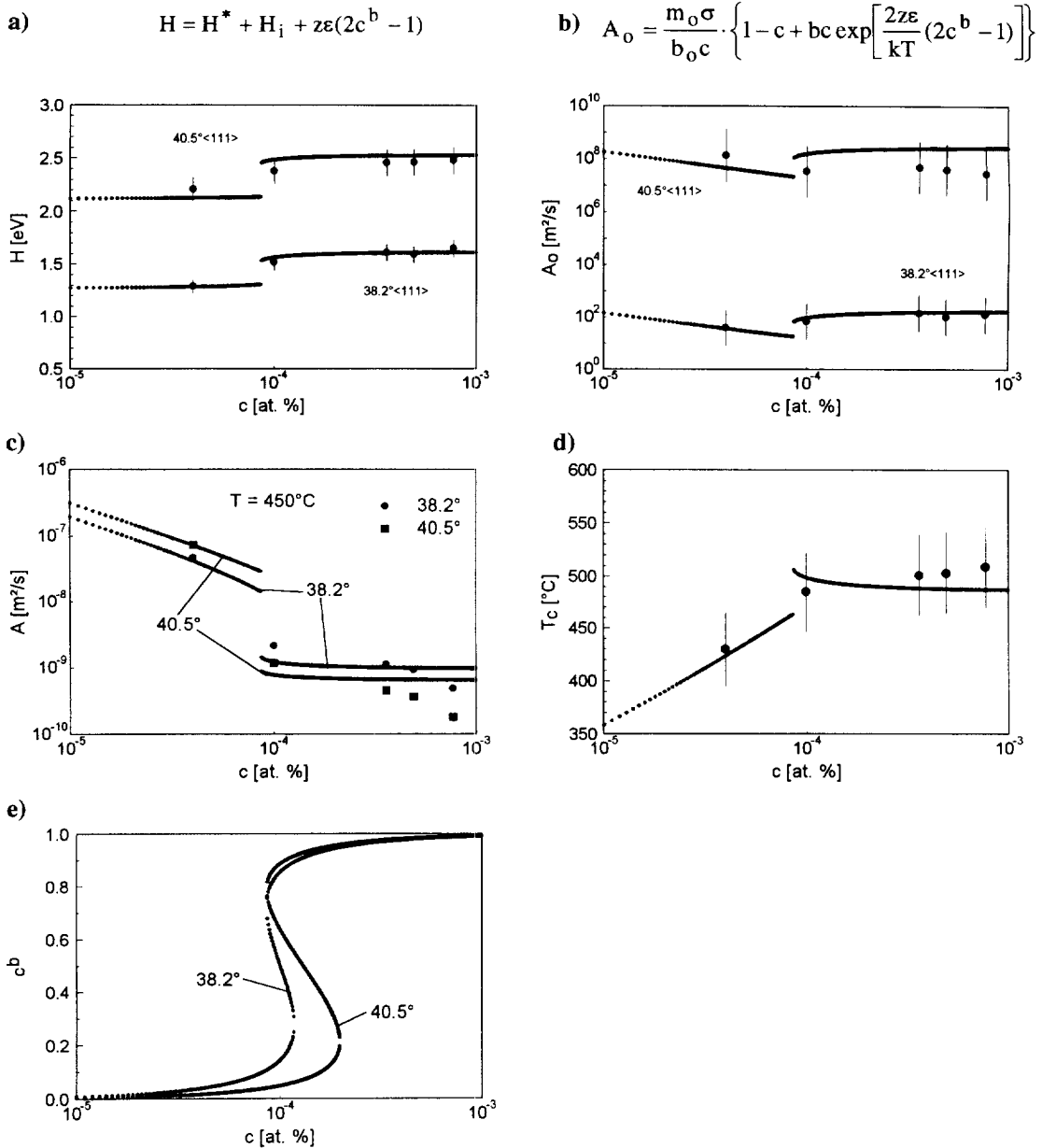


Fig. 12. Experimental data (points) and results of calculations (lines) based on equation (27) for two grain boundaries. Dependence of (a) activation enthalpy H ; (b) preexponential factor A_0 ; (c) boundary mobility A ; (d) compensation temperature T_c ; (e) impurity concentration in the boundary c^b on the bulk impurity content c . Used parameters for $38.2^\circ <111>$ boundary: $H^* = 0.6$ eV, $H_i = 0.84$ eV, $(z\varepsilon) = 0.17$ eV, $(m_0\sigma) = 7.10 \cdot 10^{-5}$ m^2/s , and for $40.5^\circ <111>$: $H^* = 1.5$ eV, $H_i = 0.82$ eV, $(z\varepsilon) = 0.21$ eV, $(m_0\sigma) = 90$ m^2/s .

was taken to be $B_0 = 5$). The best agreement between theory and experiment for the concentration dependence of boundary mobility was found for the isotherm, which takes into account a difference of the partial areas of the components in the boundary with $\beta = 0.05$ and the fitting parameters as given in the caption of Fig. 13. This becomes particularly obvious from Fig. 13(c). It is interesting that the fit parameter $m_0\sigma$ for the $\Sigma 7$ boundary amounts to $m_0\sigma = 3 \times 10^{-4}$ m^2/s . The term $m_0\sigma$ rep-

resents the reduced mobility of the boundary in the pure matrix. If boundary migration would proceed by the transfer of individual atoms across the boundary from the shrinking to the growing grain, then m_0 ought to follow simple rate theory as shown by Turnbull [14], i.e. $m_0\sigma \cong 10^{-5}$ for Al. For the same reason the activation energy for a jump across the boundary ought to be comparable to the activation energy of grain boundary diffusion, i.e. for Al in the range of 0.6–0.7 eV for the $\Sigma 7$

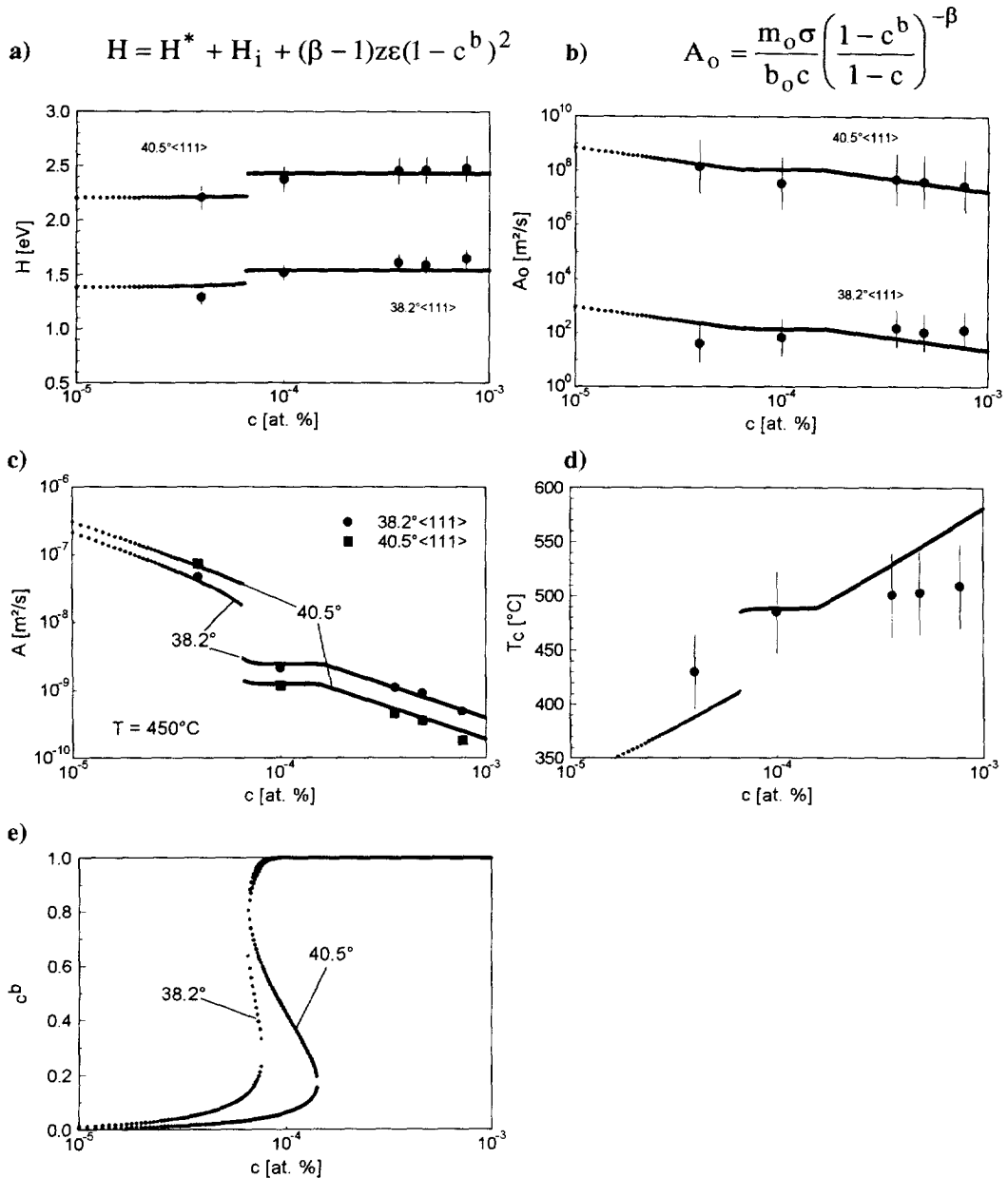


Fig. 13. Experimental data (points) and results of calculations (lines) based on equation (28) ($\beta = 0.05$) for two grain boundaries. Dependence of (a) activation enthalpy H ; (b) preexponential factor A_0 ; (c) boundary mobility A ; (d) compensation temperature T_c ; (e) impurity concentration in the boundary c^b on the bulk impurity content c . Used parameters for $38.2^\circ\langle 111 \rangle$ boundary: $H^* = 0.68$ eV, $H_i = 0.86$ eV, $(z\epsilon) = 0.17$ eV, and for $40.5^\circ\langle 111 \rangle$: $H^* = 1.57$ eV, $H_i = 0.86$ eV, $(z\epsilon) = 0.24$ eV.

boundary. Obviously, the motion of the special boundary $\Sigma 7$ is reasonably described in the framework of this simple theory, and the experimentally observed deviations of H^* and A_0 from rate theory can be attributed to the effect of segregated impurities according to the theory outlined above. Non-special boundaries, in this case the $40.5^\circ\langle 111 \rangle$ boundary behave quite differently: both activation enthalpy for grain boundary motion and preexponential reduced mobility factor are much

higher (even orders of magnitude for $m_0\sigma$) than expected for grain boundary motion caused by the exchange of individual atoms across the boundary. This indicates that the mechanism of grain boundary motion at least in this non-special boundary is different from the migration of special boundaries. In fact, the magnitude of activation energy and preexponential as well as other experimental results [8] hint at a correlated or cooperative motion of atoms during boundary migration.

Another interesting result is the different dependence of preexponential mobility factor and activation enthalpy on impurity concentration. While the preexponential factor tends to decrease with rising impurity concentration, the activation enthalpy increases with higher concentration. Commonly, the activation enthalpy H and preexponential factor A_0 for grain boundary migration are linearly related (compensation effect)

$$H = kT_c \ln A_0 + M \quad (20)$$

(T_c —compensation temperature, M —constant).

This is at variance with the trend observed in the current experiments with rising impurity level. Evidently the contradiction can be interpreted in terms of a concentration dependent compensation temperature T_c . If T_c can be understood as the equilibrium temperature of a structural phase transition in the boundary to a close metastable state, as proposed recently [22], it is obvious that the corresponding equilibrium temperature ought to depend on composition, as much as the transus temperature of a phase transformation depends on composition. However, a concentration dependence of T_c substantiates that impurities do not only affect grain boundary motion by impurity drag but also by a structural change of the boundary, which in turn again affects mobility.

Although the activation enthalpies of both the special and non-special boundary depend on impurity concentration [Figs 12(a) and 13(a)] they remain vastly different in magnitude with $H(\text{random}) > H(\text{special})$. This may be associated with different mechanisms of grain boundary migration irrespective of material purity.

For $< 100 >$ tilt boundaries, however, it was shown that the activation enthalpy of random boundaries strongly varies with changing impurity concentration, while the activation enthalpy of special grain boundaries essentially remained unaffected in an impurity range $10^{-7} \leq c \leq 10^{-4}$ [3, 4]. Recently, the current authors proposed to attribute this behavior to the different segregation behavior of special and non-

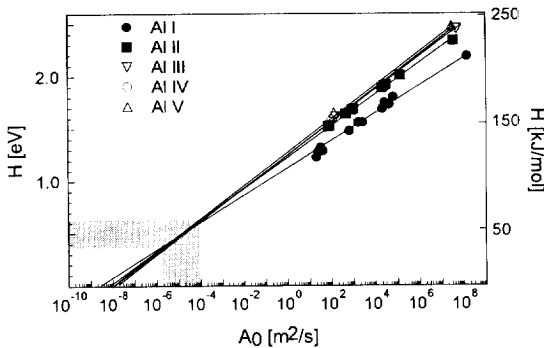


Fig. 14. Compensation lines for $< 111 >$ tilt grain boundary migration in pure aluminium with different total impurity concentration.

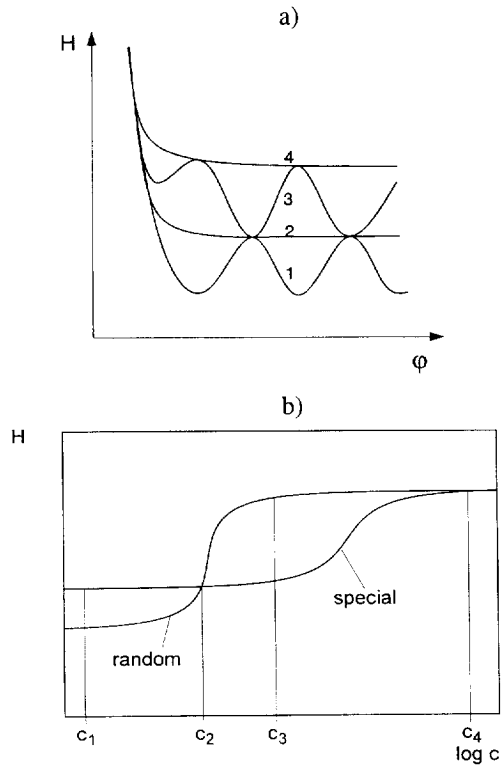


Fig. 15. Effect of materials purity on misorientation dependence of activation enthalpy for grain boundary mobility: (a) schematic misorientation dependence $H(\phi)$ for differently pure material: 1—completely pure material, 2—ultra high purity, 3—high purity, 4—low purity [24]; (b) computed dependence of activation enthalpy on impurity concentration for special and random grain boundaries.

special boundaries and predicted an inverse behavior at even lower impurity concentration [Fig. 15(a)]. This was supported by calculation of Lejcek and Adamek [16], who decomposed the activation enthalpy into intrinsic, segregation and mixing terms. The approach proposed in this paper can readily account for the predicted dependency by proper choice of the parameters in equations (18) or (19) as shown in Fig. 15(b). For $c_{\text{special}} < c_{\text{random}}$, $H^{\text{random}} > H^{\text{special}}$ for less pure material ($c > c_2$). At large impurity concentrations both types of boundaries tend to behave alike ($H^{\text{random}} \cong H^{\text{special}}$).

5. CONCLUSIONS

The temperature dependence of the mobility of $< 111 >$ tilt boundaries with angle of misorientation between 37 and 43° was investigated in bicrystals of differently pure aluminium in the temperature regime between 370 and 580°C . The following results were obtained:

1. The material purity has an extremely large effect on the grain boundary mobility. The impurity drag effect depends on misorientation across the

- boundary. The mobility of off-coincidence (random) grain boundaries depends more strongly on impurity concentration than the mobility of a special $\Sigma 7$ boundary.
- The migration activation enthalpy is strongly affected by both boundary crystallography and material purity. With increasing impurity content the activation enthalpy rises for special boundaries as well as random boundaries, in contrast to the prediction of impurity drag theory.
 - The impurity drag theory was extended to take into account an interaction of impurities in the grain boundary, i.e. treating the grain boundary as a regular solution. This approach provides a reasonable agreement with experimental results on the concentration dependence of activation enthalpy and preexponential mobility factor. It was shown that at least for the special grain boundary high values of migration activation enthalpy and preexponential factor in the mobility equation can be quantitatively explained by the effect of interaction between the adsorbed atoms.
 - The magnitude of the intrinsic mobility factors to account for the experimentally observed migration rates indicates that the 40.5° $\langle 111 \rangle$ boundary moves by group processes rather than by independent jumps of individual atoms.
 - The compensation temperature was found to depend on composition.
 - The proposed theory can properly account for the concentration dependence of special and random grain boundaries as observed for $\langle 100 \rangle$ tilt boundaries.

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