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THE MOTION OF HIGH ANGLE GRAIN BOUNDARIES IN Al AND Al-ALLOYS

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ABSTRACT

The results of measurements of grain boundary motion in bicrystals of pure Al and Al alloyed with Ga and Pb are presented. A method which enables continuous tracking of grain boundary migration is presented. The dependence of grain boundary mobility on orientation, material purity and specific impurities was addressed. It was found that the maximum growth rate misorientation changes with temperature from the exact Σ7 orientation relationship to a 40.5°<111> rotation. The grain boundary mobility was shown to be an exellent measure to characterize the total impurity content of a pure material. Some abnormal kinetic properties of grain boundaries in Al doped with Ga and Al doped with Pb are reported and discussed.

1. INTRODUCTION

The motion of grain boundaries is the fundamental process of recrystallisation and grain growth. This phenomenon is of great importance because grain boundaries in polycrystal are not alike in their properties, especially in their kinetics. There is evidence that grain boundaries properties depend on grain boundary structure, i. e. on its crystallography and chemical composition. For control of microstructure during recrystallization and grain growth it is indispensible to understand the mechanisms that control grain boundary kinetics. Experiments on polycrystals can provide information on average grain boundary behaviour only, but not on the relationship between grain boundary structure and mobility. The structural dependence of boundary mobility can only be retrieved from investigations of defined grain boundaries in material with controlled purity. The current study will focus on the orientation and materials purity dependence of grain boundary mobility in aluminium bicrystals and specifically on the effect of Ga and Pb on grain boundary motion in Al.

2. EXPERIMENTAL

The experiments were carried out on high purity aluminium from different producers, namely Volhov's Aluminium Plant, Russia (hereafter referred to as Al I), Vereinigte Aluminium Werke, Germany (Al II and Al V), Pechiney, France (Al III) and Sumitomo, Japan (Al IV) (Table 1). The impurity concentration in the used materials was determined by glow discharge mass-spectrometry. The total impurity content in each material (0.4 - 7.7 ppm) was defined as the

Material	RRR	Total impurity content, ppm	Purity, declared by producer, at. %
Al I	21400	0.4	99.999
Al II	15000	1.0	99.9999
Al III	5100	3.6	99.999
Al IV	6500	4.9	99.999
Al V	11800	7.7	99.9995

Table 1. Materials notation and purity

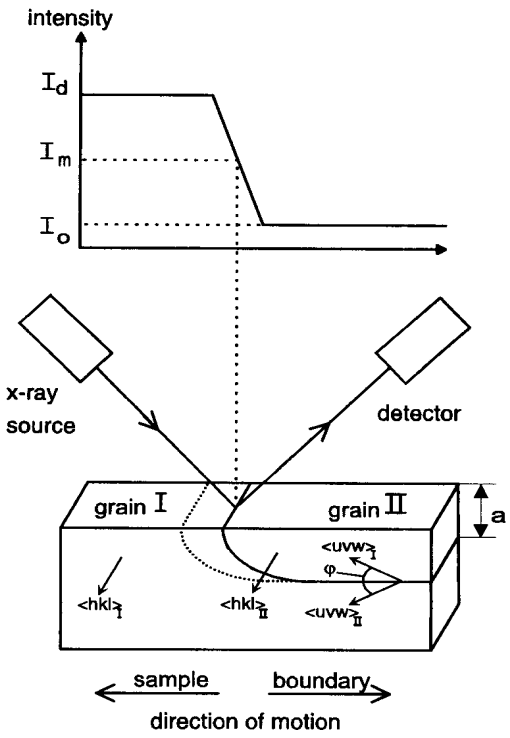

Fig. 1: Geometry of used bicrystals and measuring principle of the XICTD [3]

sum of the concentration of all found elements. The residual resistivity ratio RRR = ρ(273K)/ρ(4.2K) of the materials was measured by the method prescribed by the U.S. National Bureau of Standards.

The motion of <111> tilt boundaries with misorientation angles in the vicinity of the special misorientation Σ7 (φ = 38.2°) was studied. To measure the grain boundary mobility, the motion of grain boundaries under the action of a constant driving force was recorded (Fig. 1). The driving force was provided by the surface tension of a curved grain boundary: $p = \sigma/a$, where σ is the grain boundary surface tension, and a the width of the shrinking grain. It is particularly stressed that the boundary remains self-semilar during its motion. Details of bicrystal growth and sample preparation are given elsewhere [1, 2]. The velocity of grain boundary motion was measured using a specially designed X-ray device for continuous tracking of the moving grain boundary (XICTD) with an accuracy of better than 2% [3]. For the measurement of grain boundary motion the sample, which contains two differently oriented crystals was mounted such that under the incident X-ray beam one crystal is in Bragg-position while the other is not. A scan with X-ray beam along the sample surface resulted in an intensity distribution as shown in Fig. 1. The maximum intensity I_d is recorded as long as the the X-ray spot is entirely located on the surface of grain I. When the X-ray spot has completely moved over to grain II, the detected intensity attains the value I_o. The boundary position can be associated with the position, where the intermediate intensity $I_m = (I_o + I_d)/2$ is detected. When the boundary moves, the sample is concurrently displaced 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.

During the experiment the boundary displacement is recorded. Its derivative with regard to time is the velocity v of grain boundary motion, which is related to the driving force p by the boundary mobility $m = v / p$. For convenience we use the reduced boundary mobility

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

where H is the activation enthalpy of migration and A_0 the pre-exponential mobility factor. In the following we refer to it as mobility for brevity.

3. RESULTS

3.1. Orientation Dependence of Grain Boundary Motion

It was already shown by Aust and Rutter [4] and Shvindlerman et al. [5-7] that the mobility of tilt grain boundaries depends on axis <*hkl*> and angle φ of misorientation. Studies of the grain bounda-

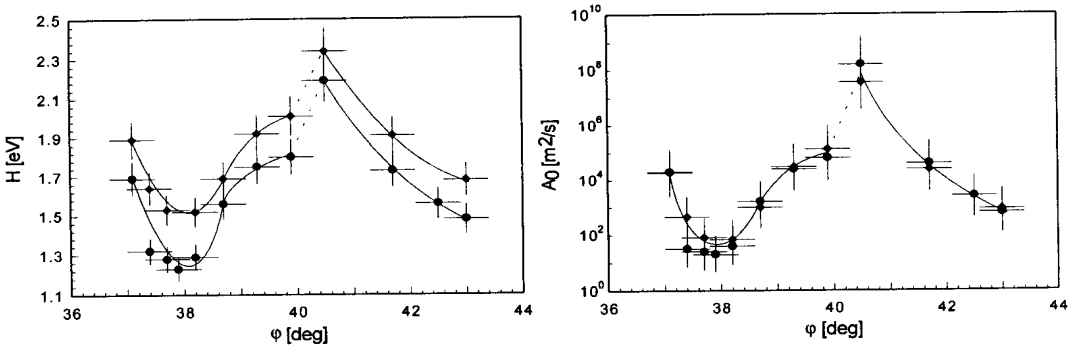

Fig. 2: Activation enthalpy H an preexponential factor A_o for <111> tilt boundaries in pure Al of different origin (● - Al I; ◆ - Al II)

ry mobility in Al bicrystals [5] have shown that tilt grain boundaries with <111> rotation axis have the highest mobility. Grain boundaries with a highly periodic coincidence structure (so called low Σ CSL or special boundaries) were found to move faster than off-coincidence (random) boundaries, and in Al the special Σ7 (38.2°<111>) tilt boundary was identified as the absolutely fastest.
However, from growth selection experiments of Lücke et al. [8-9] it is known that the fastest boundary is not the Σ7 boundary, but random boundary with rotation angle of slightly more than 40°.
We investigated the misorientation dependence of grain boundary mobility on a fine scale in the angular interval 37°-43°<111> with angular spacing 0.3°-0.6°. The experiments reveal that both the activation enthalpy and the preexponential factor are at maximum for misorientation angle φ=40.5° and at minimum for the exact Σ7 orientation (Fig. 2). The mobility of boundaries with different misorientation angle have a different temperature dependence, and there is a temperature, the so-called compensation temperature T_c, where the mobilities of the boundaries of differently misoriented grains are the same. As a result, for $T>T_c$, the mobility is higher for grain boundaries with higher activation energy, in particular it is at maximum for φ=40.5°, while for $T<T_c$ the exact Σ7 boundary moves fastest (Fig. 3). This result easily explains the apparent contradiction between growth selection experiments and recrystallization experiments. The problem resulted only from the wrong tacit assumption that the preexponential factor is essentially independent of misorientation so that only the activation enthalpy controls mobility. Growth selection experiments were conducted at very high temperatures (above 600°C), i. e. in the temperature regime, where, according to results of the current study, the mobility of the 40.5<111> boundary due to high preexponential factor is the

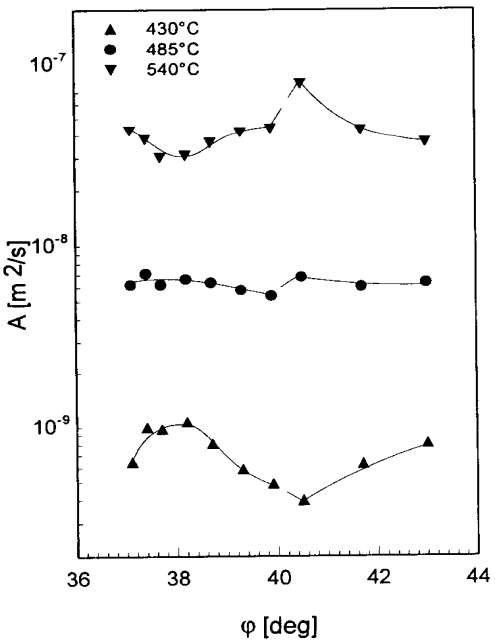

Fig. 3: Mobility of <111> tilt grain boundaries in pure Al (Al II)

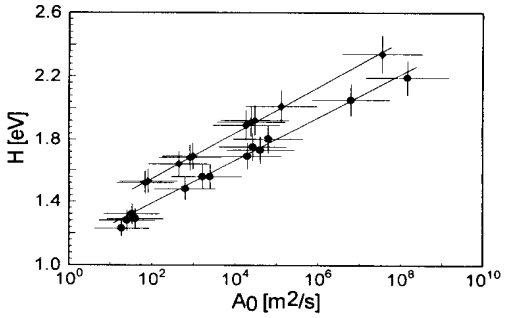

Fig.4: Dependence of migration activation enthalpy on preexponential mobility factor for <111> tilt grain boundaries in Al I (●) and Al II (◆).

highest. The reason for the different maximum mobility orientations in different temperature regimes is obviously the orientation dependence of both, the activation enthalpy and the preexponential factor, and the linear relationship between H and $log\ A_o$ - the compensation effect (Fig. 4).

3.2. Effect of Materials Purity on Grain Boundary Motion

It is well known that material purity has a great influence on grain boundary motion. Grain boundary motion is almost always slowed down by solute impurities. But much less is known on how solute atoms affect the activation enthalpy of grain boundary migration and the preexponential mobility factor and how much this effect depends on grain boundary crystallography. As expected, in our experiments impurities were found to reduce grain boundary mobility (Fig. 5). But in contrast to the impurity drag theory [10, 11] the mobility does not decrease due to a reduction of the preexponential factor, but due to a considerable rise of the activation enthalpy. The preexponential factor was found to be practically independent of impurity concentration (Figs. 2 and 6). Also, a consequence of different purity is the change of the compensation temperature which rises distinctly with increasing impurity content (Figs. 4 and 6).
As a result, the migration activation enthalpy is strongly affected by both, the boundary crystallography and material purity. However, in the former case the preexponential factor A_o rises by several orders of magnitude with increasing H, while in the latter case A_o remains at the same level. Therefore, in the investigated impurity concentration interval the preexponential factor A_o was found to be much less sensitive to the material purity than to a change of the misorientation angle. This result allows to conclude that the observed orientation dependence of mobility (Fig. 3), determined by both H and A_o, does not only reflect the different segregation behavior of special and random boundaries, as frequently proposed [4], rather it provides evidence for an intrinsic dependence of grain boundary mobility on grain boundary structure.
The experiments reveal that the grain boundary mobility can be utilized as a measure for the total impurity content of a metal. We have investigated the grain boundary mobility of high purity Al of different producers, i. e. of different origin and, therefore, contaminated with trace elements in different concentrations. In contrast to the residual resistivity ratio (RRR) (Table 1), which is commonly used to characterize the material purity, the mobility decreases monotonously with increasing impurity content (Fig. 5). Moreover, the mobility is much more sensitive to the solute content than the electrical resistivity: for an impurity content rising by a factor of about 20, the RRR varies by a factor of 4, while the mobility (compared at 450°C) decreases by more than two orders of magnitude.

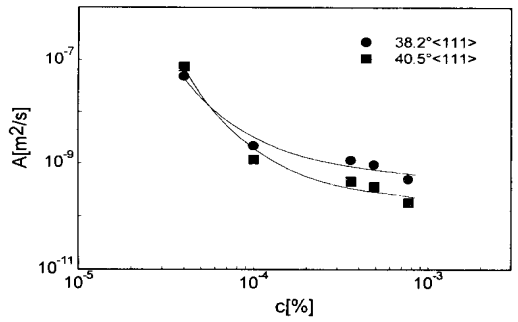

Fig. 5: Dependence of grain boundary mobility on total impurity content in pure Al

3.3. Acceleration of Grain Boundary Motion in Al by Ga

All known experiments on bicrystals and polycrystals confirm that solute atoms reduce the rate of boundary motion. There are, however, remarkable exceptions to the general rule that. One example is the grain boundary motion in Al doped with minor amounts of Ga. Our experiments were carried out on bicrystals of both pure Al (Al III) and the same Al doped with 10 ppm Ga. The grain boundary mobility is found to be much higher in Al + 10 ppm Ga than in pure Al over the entire investigated temperature range for both 38.2° and 40.5°<111> tilt boundaries (Fig. 7). Addition of 10 ppm Ga effectively increases the mobility of both boundaries, but modifies the activation parameters differently. For the 38.2° (Σ7) boundary H and A_o increase, while they decrease for the 40.5° boundary. The orientation dependence of grain boundary mobility is strongly reduced, but not entirely removed. We interpret these results as a change of mechanism of grain boundary migration owing to a change of boundary structure, such that a prewetting phase transition occurs and a thin layer of a Ga-rich phase forms in the boundary.

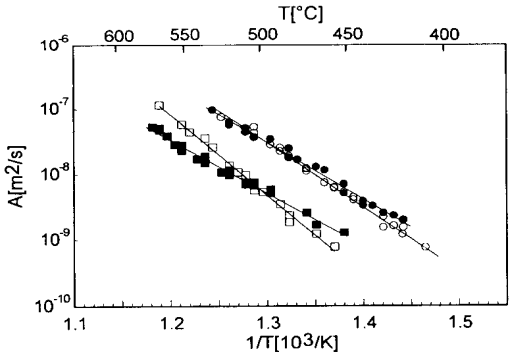

Fig. 7: Temperature dependence of mobility of 38.2° (●, ■) and 40.5°(○, □) <111> tilt grain boundaries in pure Al (□, ■) and Al+10 ppm Ga (○, ●).

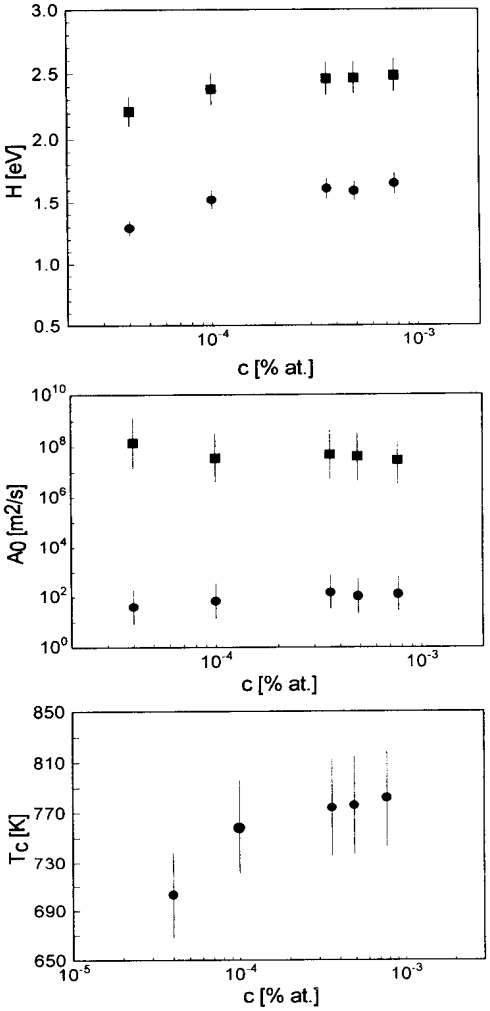

Fig. 6: Dependence of activation enthalpy H, preexponential factor A_0 and compensation temperatures T_c in pure Al for 38.2° (●) and 40.5° (■) <111>-tilt grain boundaries.

3.4. Effect of Pb on Grain Boundary Motion in Al

An other prominent example of unusual phenomena of grain boundary motion is the effect of Pb on boundary migration in Al. According to modern data a solubility of Pb in Al is extremely small [12]. But in accordance with [13] at the monotectic temperature(658.5°) it is about 0.025 at.%. However, in a systematic investigation into the influence of material purity and specific impurities on grain boundary motion we found that the

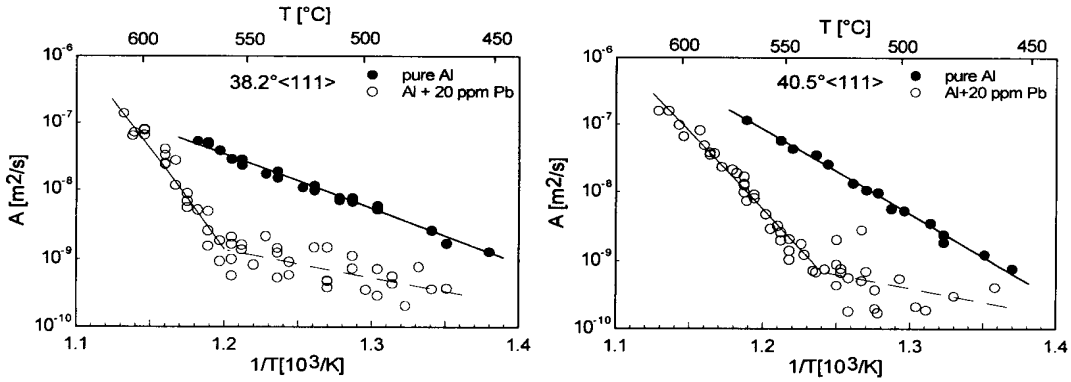

Fig. 8: Temperatures dependence of grain boundary mobility in pure Al and Al + 20 ppm Pb

effect of 20 ppm Pb added to pure Al is drastically different from the usual effect of solutes on grain boundary motion. We investigated again the high mobility boundaries Σ7 and 40.5°<111> as referred to above. The temperature dependence of grain boundary mobility in Al doped with Pb revealed that for a given misorientation, there is a temperature, at which the migration activation enthalpy and preexponential mobility factor rise drastacally (Fig. 8). We intepret this result as a wetting phase transition in the grain boundary. The transition temperature is higher for the special Σ7 grain boundary. The unstable motion of grain boundaries in the low temperature regime is attributed to a boundary motion dragged by small drops of liquid lead. After the transition point owing to a wetting of grain boundary by liquid lead and formation of a lead layer on it, the mechanism of grain boundary motion changes drastically.

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