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In-Situ Observations of Grain Boundary Migration

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ABSTRACT

The X-ray Interface Continuous Tracking Device is introduced which is capable of on-line tracking of grain boundary motion and thus, provides information on grain boundary mobility. The grain boundary velocity was found to change in proportion to the driving force. The orientation dependence of mobility does not only affect the activation enthalpy of grain boundary motion, but also the preexponential mobility factor. This causes the exact Σ7 boundary to move fastest at low temperatures, however, the 40.5°<111> boundary is most mobile at high temperatures. As expected, impurities were found to reduce the grain boundary mobility, but the mobility can also be enhanced by the addition of small amounts of Ga to pure Al. In-situ HRTEM observations of grain boundary motion in thin film Au bicrystals are presented, which reveal the mechanism of mass transfer across the grain boundary during its migration.

1. INTRODUCTION

Grain boundary migration (GBM) is the fundamental process of recrystallization and grain growth. Because of the significance of these microstructural phenomena for the processing of metallic materials, more than 100 years have been dedicated to the research on these phenomena, hence one ought to expect that the mechanisms of GBM are well understood. However, the contrary is closer to the truth. Despite extensive efforts to tackle this problem in the past, there is disappointingly little understanding of the mechanisms of grain boundary motion to date. First studies of grain boundary migration utilized the growth of grains in polycrystals during either recrystallization or grain growth. Such experiments can provide information only on average grain boundary behaviour but not on the relationship between grain boundary structure and mobility [1]. Aust and coworkers [2] used deformed Cu single crystals to study grain boundary motion. The driving force was supplied by deformation induced „striations", and the authors reported an orientation dependence of grain boundary mobility. However, it was not clear how the deformation structure would interfere with grain boundary structure and thus, affect mobility. Therefore, experiments on bicrystals with curved grain boundaries were designed [3-5] and surprising results were obtained. In particular the experiments by Rath and Hu [5] on Al bicrystals have contributed to confusion, since they seemed to disprove even the fundamental theoretical prediction that the velocity of a grain boundary must be proportional to the driving force, or

$$\upsilon = mp \qquad (1)$$

Rath and Hu contended that their result suggested some power law $\upsilon \sim p^n$ with n being as high as 12, depending on unspecified specimen conditions, most likely on its chemistry. A power law dependence

is difficult to reconcile with fundamental theoretical considerations of grain boundary migration and, therefore, would preclude any systematic analytical treatment of the problem[1]. Thus, it was concluded that the measurements did not represent steady state motion, but a transition from an impurity dragged to a freely moving boundary. It is quite obvious that this interpretation is unrealistic, since the boundary cannot always remain in a transition state for extended time intervals and different temperatures. Shvindlerman and co-workers [8] were the first to recognize that the experimental results of Rath and Hu were impaired by grooving phenomena and, therefore, not relevant to stationary genuine grain boundary migration. Moreover, they proved that for proper experimental conduct the velocity of a grain boundary indeed is proportional to the driving force (Fig. 1). The latter result reconciles exponents and fundamental concepts of GBM and allows to systematically study the dependency of grain boundary mobility on variables of interest, like misorientation, grain boundary plane, impurity content, temperature, pressure, etc.

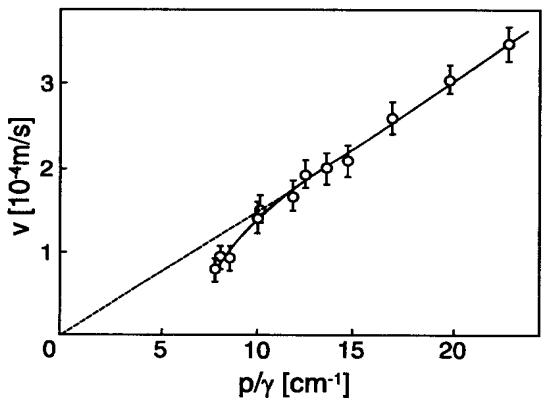

Fig. 1: Dependence of grain boundary migration rate on driving force.

The major experimental problem to overcome is the interference of grain boundary motion with the observation procedure. In a conventional experiment the sample containing the grain boundary under investigation is subjected to an annealing treatment and the displacement of the boundary is measured after the cool-down. This inevitably leads to grooving of the boundary due to condensation of thermal vacancies and, therefore, to groove dragging upon reheating with all the unwanted side-effects addressed above. A proper experimental investigation, therefore, requires an on-line measurement of grain boundary migration at temperature and suppression of grooving. This rules out optical tracking of the grain boundary except for optically anisotropic materials. Below we shall introduce an experimental method for on-line tracking of grain boundaries and its application to problems relevant to recrystallization and grain growth.

While on-line tracking of grain boundary motion provides information on the dependence of grain boundary mobility on variables of interest, it can yield only indirect conclusions on the mechanism of migration. To address the atomistics of mass transfer in the boundary, we employed high resolution electron microscopy to reveal the exchange of lattice sites between the adjacent grains and to probe potential preferred jump sequences or coordination of site exchange. Only for sake of completeness it is mentioned that these experimental investigations are complemented by a third activity, namely molecular dynamics simulations to associate the observed mechanisms with atomistic configurations and their evolution. In this contribution, however, we shall confine our considerations to experimental results.

[1] At most an exponent n=2 for the case that the mechanism of migration also depends on the driving force could be accounted for steady state grain boundary migration [6,7].

2. ON-LINE TRACKING OF GRAIN BOUNDARY MIGRATION

2.1 The X-ray Interface Continuous Tracking Device (XICTD)

Since a grain boundary separates two differently oriented crystalline volumes, X-ray diffraction can be utilized for locating and tracking the grain boundary position. For defined and maintained grain boundary geometry during the measurement, bicrystal specimens are being used, which contain a curved tilt grain boundary (Fig. 2). This boundary geometry offers the advantage that the boundary remains self-similar during migration and that it moves under the action of a constant driving force $p=\sigma/a$, where σ is the grain boundary surface tension and a is the width of the consumed grain and thus, can be adjusted according to needs. For the measurement of grain boundary motion the bicrystal (Fig. 2) was mounted onto the goniometer such that one grain was in Bragg-position while the other was not. A scan with the X-ray beam along the sample surface resulted in an intensity distribution as shown in Fig. 3. The boundary position can be associated with the position where the intensity $I_M = (I_0 + I_U)/2$ is recorded. When the boundary moves, the sample must be concurrently displaced such that the reflected X-ray intensity remains constant during the measurement. During the measurement both the boundary position and the boundary velocity were displayed on the computer screen. At a given temperature and driving force the boundary was found to move at a constant velocity, from which the mobility can be calculated according to eq. (1). For sake of convenience we shall use the reduced mobility $A = m\sigma = A_0 \exp(-Q/kT)$ in the following and for brevity refer to it as mobility. Details of the experimental setup, accuracy and performance are given elsewhere [9,10]. It is particularly stressed that the observed steady state grain boundary migration rate was not affected by grooving. Mullins [11] and Brokman [12] have shown that a grain boundary may also move in a steady state controlled by groove dragging. This, however, would require a very small specimen thickness (thin film) or a very low migration rate (or driving force, respectively). In fact, to

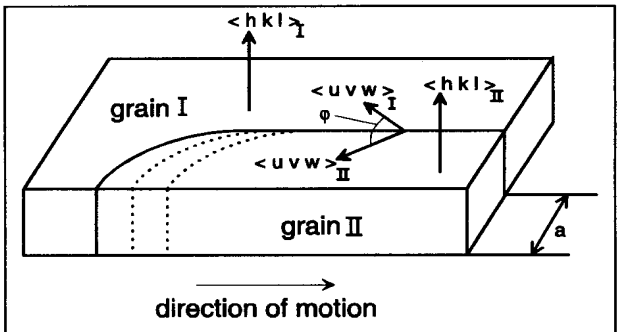

Fig. 2: Crystallography of used bicrystals.

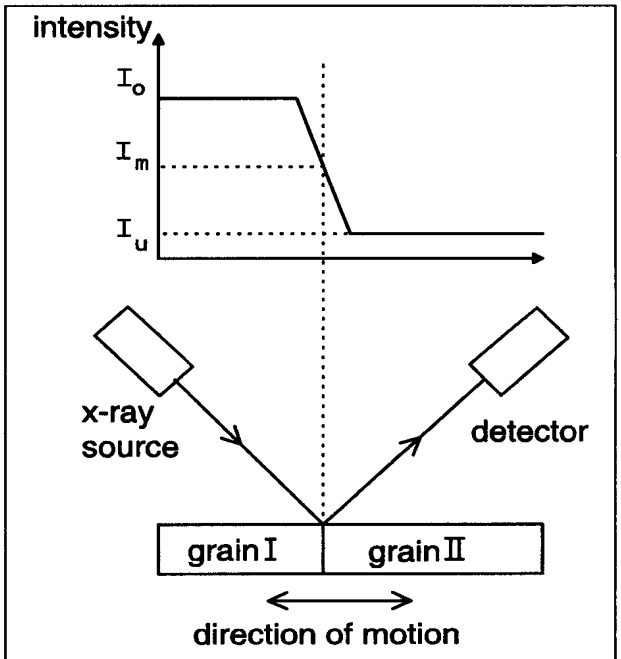

Fig. 3: Measuring principle of the XICTD.

obtain a significant influence by groove dragging would require a specimen thickness of less than 10^{-3}cm. In our experiments the boundary moved much too fast for groove dragging be sustained, because the driving force was at least an order of magnitude higher than the drag force exerted by the groove on the boundary. This was achieved by the large specimen thickness (several mm) and the small radius of curvature of the moving boundary. Moreover, the experiments were conducted in a nitrogen gas atmosphere to conserve the oxide layer on the specimen surface. Once the boundary was detached from the groove it was protected from regrooving by the oxide layer owing to suppression of thermal grooving. The test program would carefully avoid to decrease the temperature in order to prevent grooving by condensation of thermal vacancies and thus potential locking of the boundary.

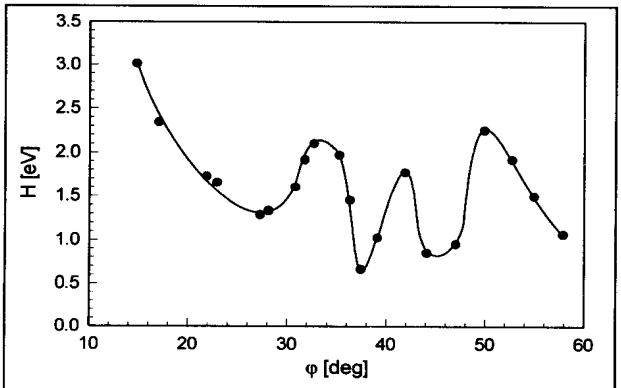

Fig. 4: Dependence of activation enthalpy of GBM on misorientation angle for <111> tilt boundaries in Al.

2.2 Orientation dependence of grain boundary mobility

Shvindlerman et al. [13-16] have already shown for Al, Zn and Sn that except for ultrapure material, grain boundary mobility depends on misorientation of the adjacent grains (Fig. 4) as defined by axis <hkl> and angle ω of rotation: ω<hkl>. Evidently, highly periodic coincidence boundaries (low Σ boundaries or special boundaries) were found to exhibit a higher mobility than off-coincidence (non-special or random) boundaries, and the authors identified as the fastest boundary the Σ7(38.2°<111>) tilt boundary. These findings confirmed recrystallization experiments by Aust and Rutter [17] in Sn-Pb alloys of different composition. However, both observations are at variance with results obtained by growth selection experiments, which provided unambiguous evidence that the fastest boundaries were not the Σ7 boundaries, but random boundaries with angle of rotation of slightly more than 40° [18,19]. Since the original experiments of Shvindlerman et al. were conducted only with rather large angular intervals of misorientation, we investigated the orientation dependence of GBM on a fine scale in the angular range 37°-43°<111> with angular spacing of 0.4° (Fig. 5). The experiments reveal that the mobility of differently oriented boundaries do have different temperature dependencies, such that at low temperatures (T<430°C) the exact Σ7 boundary moves fastest, while at high temperatures the 40.5°<111> boundary is most mobile. This is due to the high activation enthalpy H and the high preexponential factor A_0 of the 40.5°<111> boundary that disfavors its mobility $A = A_0 \exp(-H/kT)$ at lower temperatures[2]. Therefore, at the high temperatures needed for growth selection experiments the 40.5°<111> boundary is orders of magnitude faster than the Σ7 boundary, while at low temperatures, where recrystallization and GBM experiments are commonly carried out, the exact Σ7 boundary prevails in the mobility contest. As a result, both experiments were correctly conducted and interpreted, and for the first time recrystallization and growth selection data can be reconciled. 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.

[2] The correlation of activation enthalpy and preexponential factor is a fundamental grain boundary property and will be addressed in the contribution by Shvindlerman et al. in this volume

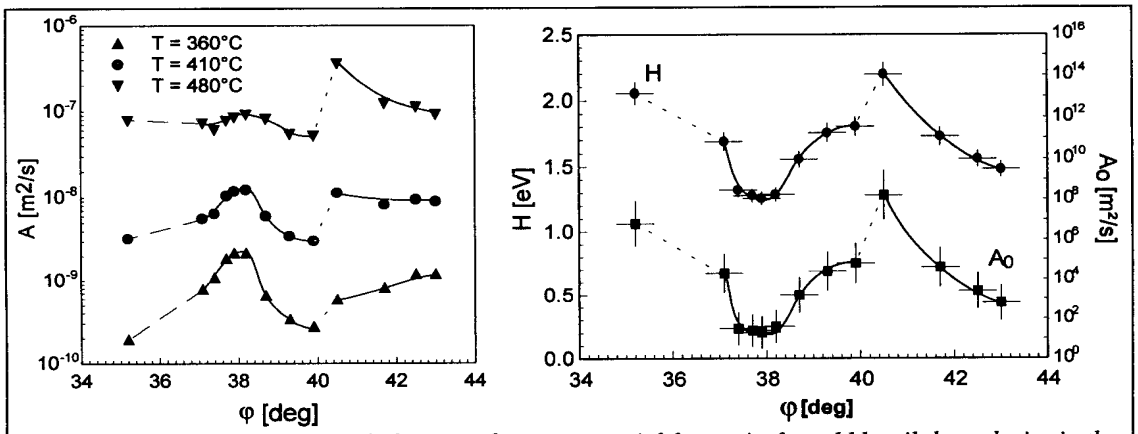

Fig. 5: Mobility A, activation enthalpy H and preexponential factor A_0 for <111> tilt boundaries in the angular range between 37° and 43°.

2.3 Effect of impurities on GBM

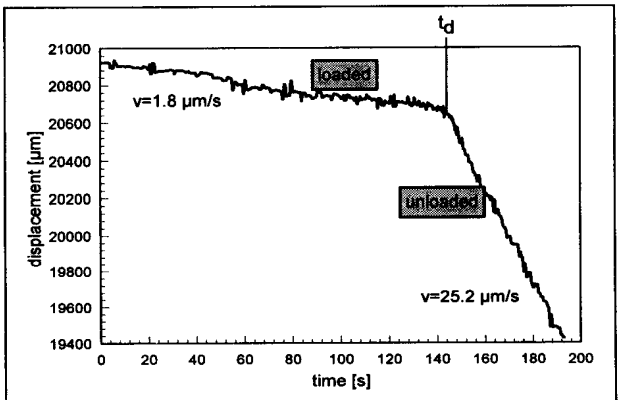

Fig. 6: Grain boundary displacement with annealing time at a critical temperature. The boundary changes from a dragged to a free motion.

It is a common experience that recrystallization and grain growth kinetics are slowed down by addition of alloying elements to a pure metal. This is accounted for by the impurity drag theory [20,21], which predicts a segregation of impurities to the moving boundary and thus, a retarding force on the grain boundary, which becomes apparent as a reduced grain boundary mobility. Measurements of grain boundary mobility not only confirm this general tendency, but can also reveal the sudden but stable transition from the loaded to the unloaded state of the moving grain boundary, when measurements are conducted in the critical temperature regime (Fig. 6). This experimental result also substantiates that the unzipping of the boundary from its impurities leads from one stable state to another stable state and does not generate oscillations between the two states, as originally claimed to explain nonlinearity of grain boundary migration rate with driving force, i.e. the transition regime is not a potential third metastable mobility state. As a matter of fact 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 different trace elements. The mobility decreases monotonously with increasing impurity content, which was determined by glow dischange mass spectrometry (Fig. 7). It is interesting to note in this context that the residual electrical resistivity ratio is a much less reliable measure of the impurity content, in particular in case of any tendency among the impurities to form compounds [22].

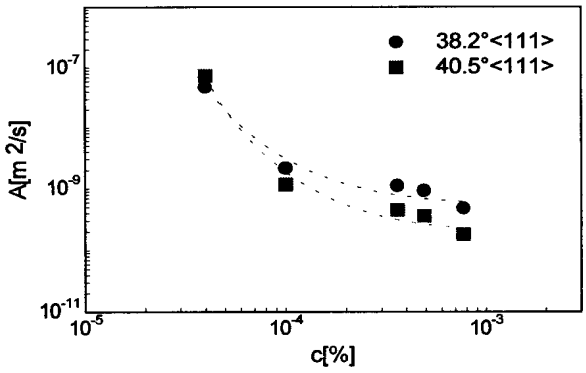

Fig. 7: Dependence of grain boundary mobility on total impurity content in pure Aluminium.

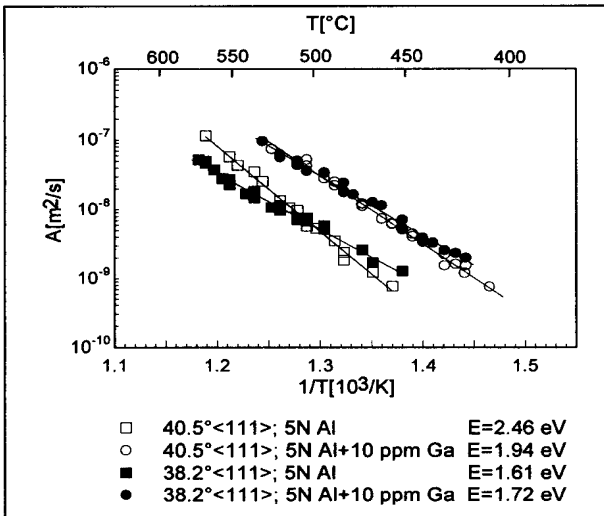

Fig. 8: Temperature dependence of grain boundary mobility for pure Al and Al+10 ppm Ga of Σ7 and 40.5°<111> boundaries.

There are, however, remarkable exceptions to the general rule that can cause surprising results. A prominent example is Aluminium doped with minor amounts of Gallium. In contrast to other alloying elements Ga raises the mobility and thus accelerates grain boundary migration and, as a consequence, speeds up recrystallization kinetics. The magnitude of mobility increase is remarkable, but different for different grain boundaries (Fig. 8). We investigated again the high mobility boundaries Σ7 and 40.5°<111> as referred to above. Addition of the same amount of Ga to both boundaries effectively increases the mobility of both boundaries but modifies the activation parameters (A_0, H) differently, namely such that their difference diminishes substantially. Hence, preexponential factor and activation enthalpy decrease for the 40.5°<111> boundary, while the same parameters increase for the exact Σ7 boundary. Nevertheless, an orientation dependency remains, although much less pronounced than in the undoped material. We interpret these results as a change of grain boundary structure, such that a prewetting phase transition occurs in the boundary and a thin film of a Ga-rich phase forms in the boundary. As a result the grain boundary structure changes from a narrow- to a wide-type boundary, which also affects the mechanisms controlling grain boundary migration. The remaining orientation dependence of the mobility is likely due to an orientation dependence of the detachment/attachment processes at the interfaces between Ga-film and the adjacent growing and shrinking grains, respectively. HRTEM investigations are under way to probe the existence of a Ga-rich film on the grain boundary.

3. HRTEM OBSERVATION OF GBM

To obtain information upon the atomistic mechanisms of grain boundary migration we conducted in-situ experiments in the electron microscope. It is necessary to give some explanations for the objective,

possibilities and limitations of this work. First of all it is necessary to use very thin foils or films to conduct HRTEM, and the specimen has to be kept in high vacuum possibly at elevated temperatures. Of course, these experimental conditions will promote grooving, and since the dragging force of a groove scales with d^{-1}, where d is the film thickness, grooving will strongly anchor the grain boundary. This, however, does not suppress grain boundary motion as long as the driving force is sufficiently high to overcome groove dragging. Nevertheless, the grain boundary will move very slowly owing to these unfavourable conditions. However, this slow movement is very beneficial for the HRTEM experiments. The field of view is very small in TEM, even more for HRTEM; therefore, a fast moving boundary would get out of view very fast and, therefore, preclude an observation of the atomistic transfer mechanisms, since the video camera can record the sequence only with a rate of 25 frames per second. Therefore, low temperature and strong dragging are necessary to slow down the boundary to rates in the order of <1nm/s. Also caution must be exercised with the interpretation of the HRTEM images. While the bright or dark spots of the HRTEM image are readily associated with atoms, in reality they correspond to columns of atoms through the sheet thickness. Despite the small thickness of the order of 5 nm for 200 kV operating voltage there are about 10 atoms in each column that have to be displaced to move the whole column.

The investigated specimen was a thin film bicrystal of gold prepared according to the Schober-Balluffi-technique [23], i.e. consisted of a film with a 29°<100> twist grain boundary in the midlayer plan. Upon heating the boundary develops bulges, which eventually touch the surface (Fig. 9). The thus created tilt boundaries experience a driving force to grow at the expense of the twist boundary [24]. The boundary segment under investigation in the TEM was a tilt boundary which was pinned by imperfections (bubbles) in the twist boundary. During the recorded motion the boundary moved forward and then returned to the original position like in an oscillatory motion. The sequence of video frames close to the point of return is given in Fig. 10a. It is evident that new (rows of) atoms attach to the ledges of the growing grain, while corresponding sites of the shrinking grain are removed. Again, while the sequence seems to suggest that individual atoms change from one grain to the other, it must be kept in mind that we actually observe columns consisting of several atoms. We cannot discriminate whether individual atoms move or whether a coordinated motion of columns takes place between two consecutive video frames. The lattice image at the boundary is rather blurred, which may be due to the relatively high temperature (room temperature) or due to imperfections in the row structure (vacancies or partially dismantled column). Better contrast conditions and possibly a high speed video camera should elucidate details of column structure during the fundamental migration step. This will be attempted in future experiments.

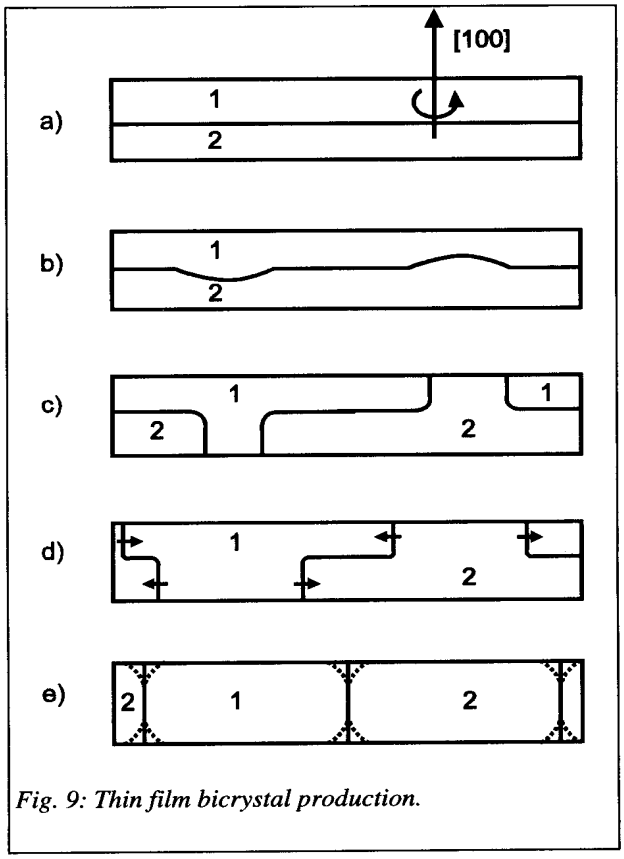

Fig. 9: Thin film bicrystal production.

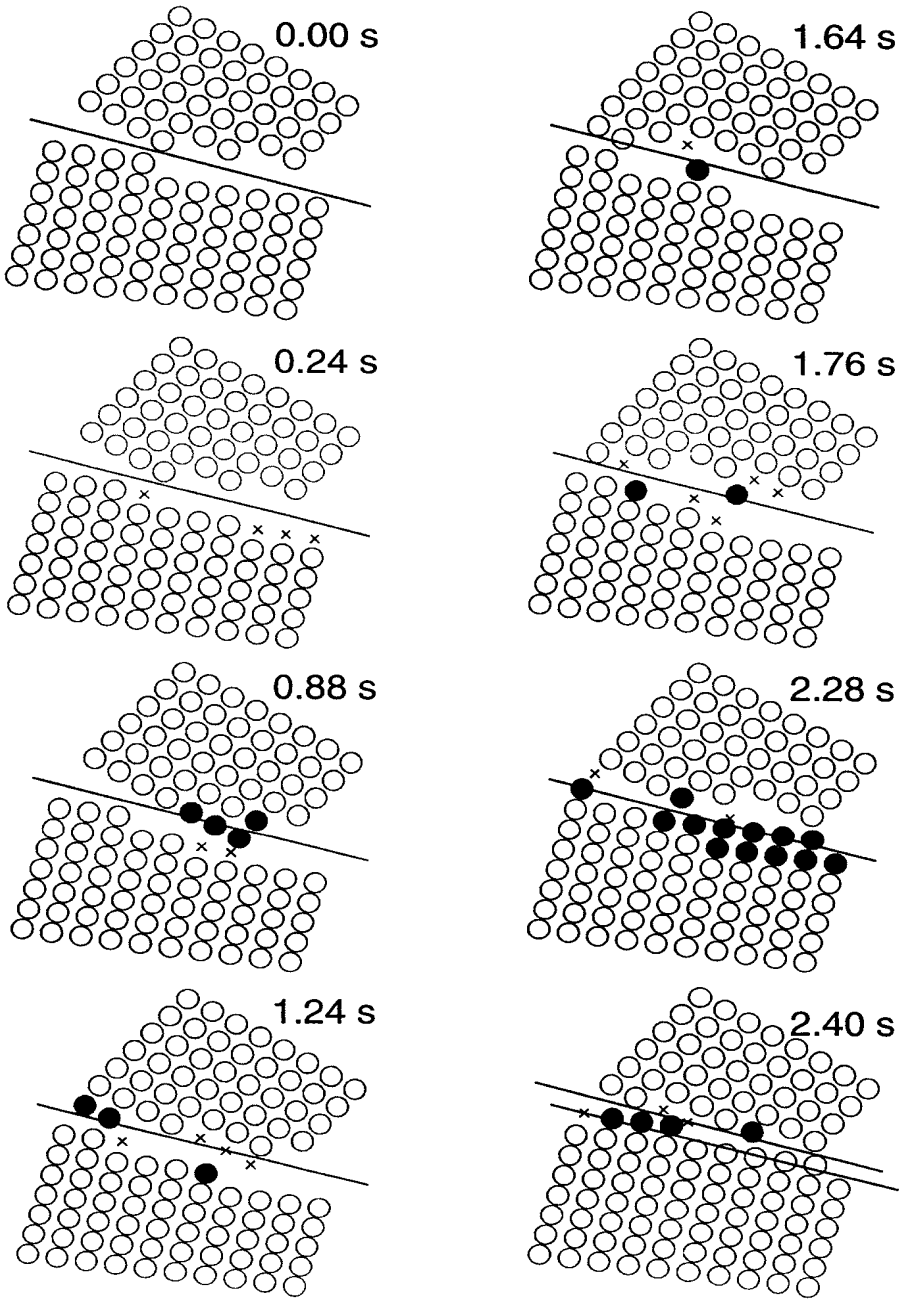

Fig. 10b: Atomic arrangements close to a moving 29°<100> boundary as extracted from the sequence of HRTEM video frames in Fig. 10a, **X** *deleted sites,* ● *created sites*

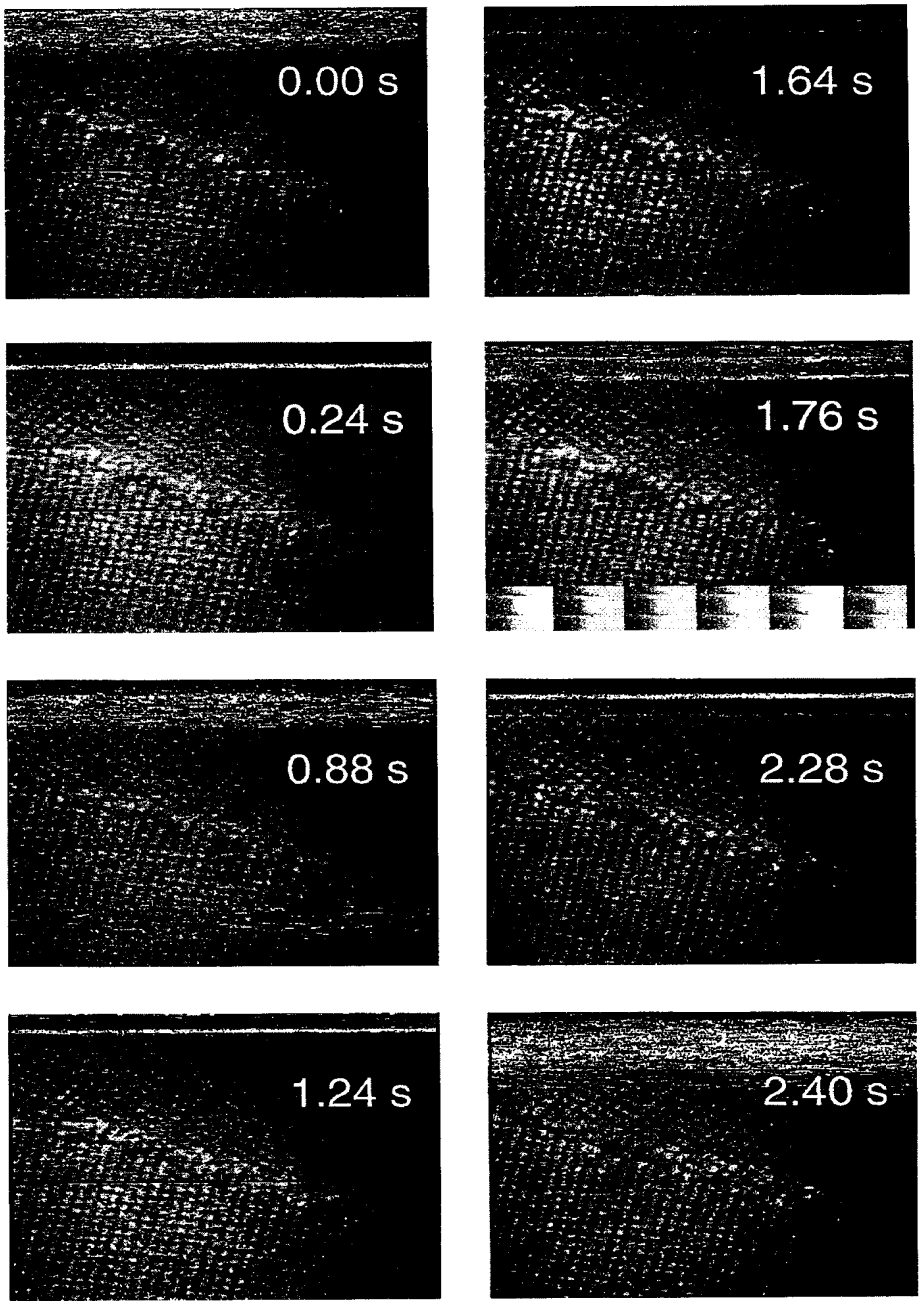

Fig. 10a: Sequence of select HRTEM video frames of grain boundary migartion in a gold thin film bicrystal

4. CONCLUSIONS

1. A new device is introduced, which allows continuous tracking of grain boundaries without interference with the migration process.
2. The boundary migration rate was found to change in proportion to the driving force.
3. The mobility depends on misorientation across the boundary, but both preexponential factor A_0 and activation enthalpy H depend on misorientation. The 40.5°<111> boundary is characterized by high values of A_0 and H and, therefore, moves fastest at high temperatures (T>430°C), while the exact $\Sigma 7$ boundary has the highest mobility at lower temperatures. This reconciles the seemingly contradictory findings of recrystallization and growth selection experiments.
4. Grain boundary mobility is affected by impurities such that the mobility decreases with growing impurity content. Surprisingly, the boundary mobility in Al increases upon minor additions of Ga. This is attributed to a prewetting phase transition in the grain boundary.
5. In-situ HRTEM investigations were conducted on boundary motion in thin film bicrystals of gold. The observed motion suggests that individual columns in boundary are dismantled and attached to the ledges of the shrinking and growing grain, respectively.

REFERENCES

[1] R.A. Vandermeer; Trans. AIME **233**, 265-267 (1965).
[2] G. Ferran, G. Cizeron, K.T. Aust; Memories Scientifiques Rev. Metallurg., **LXIV** 1067-1076 (1967).
[3] R,C. Sun, C.L. Bauer; Acta Metall. **18**, 635-638 (1979).
[4] R,C. Sun, C.L. Bauer; Acta Metall. **18**, 639-647 (1979).
[5] B.B. Rath and H. Hu; "The Nature and Behavior of Grain Boundaries", ed. H. Hu, Plenum Press, New York, 405-435 (1972).
[6] K. Lücke and G. Gottstein; Acta Metall. **29**, 779-789 (1981).
[7] D.A. Smith, C.M.F. Rae, C.R.M. Grovenor; "Grain Boundary Structure and Kinetics", ed. R.W. Balluffi, American Society for Metals, Metals Park, Ohio, 337-371 (1979).
[8] V.Yu. Aristov, V.Ye. Fradkov, L.S. Shvindlerman; Phys. Met. Metall. **45**, 83-94 (1979).
[9] U. Czubayko, D.A. Molodov, B.-C. Petersen, G. Gottstein, L.S. Shvindlerman; Mat. Sci. For. **157-162**, 125-130 (1994).
[10] U. Czubayko, D. Molodov, B.-C. Petersen, G. Gottstein, L.S. Shvindlerman; Measurement Sci. Techn., in press (1995).
[11] W.W. Mullins; Acta Metall. **6**, 414 (1958).
[12] A. Brokman, R. Kris, W.W. Mullins, A.J. Vihnkin; Scripta Met. Mat. **32**, 1341 (1995).
[13] E.M. Fridman, C.V. Kopetskii, L.S. Shvindlerman; Z. Metallk. **66**, 533 (1975).
[14] A.V. Antonov, Ch.V. Kopetskii, L.S. Shvindlerman; Phys. Met. Metall. **32**, 187-192 (1971).
[15] D.A. Molodov, B.B. Straumal, L.S. Shvindlerman; Sov. Phys. Solid State **26**, 629-633 (1984).
[16] E.L. Maksimova, L.S. Shvindlerman, B.B. Straumal; Acta Metall. **36**, 1573-1583 (1988).
[17] K.T. Aust, J.W. Rutter; Trans. AIME **215**, 119-127 (1959).
[18] G. Ibe, W. Dietz, A.C. Fraker and K. Lücke; Z. Metallk. **61**, 498-507 (1970).
[19] K. Lücke; Can. Met. Quart. **13**, 261-274 (1974).
[20] K. Lücke and H. Stüwe; "Recovery and Recrystallization of Metals", ed. L. Himmel, Interscience, New York, 171-210 (1963).
[21] J.W. Cahn; Acta Metall. **10**, 789-798 (1962).
[22] D.A. Molodov, U. Czubayko, G. Gottstein, L.S. Shvindlerman; JOM; submitted (1995).
[23] R.W. Balluffi and T. Schober; Scripta Metall. **6**, 697-706 (1972).
[24] R.M. Allen and P.J. Goodhew; Acta Metall. **25**, 1095-1107 (1977).