KINETIC PHASE TRANSITIONS ON MIGRATING GRAIN BOUNDARIES

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The kinetic phase transition on moving grain boundaries (GB) is considered. At such transition migrating GB brakes-away from the adsorbed impurity. The theory of planar and curved GB brake-away from the impurity developed. The role of various factors, such as interaction potential "impurity-GB", diffusion coefficient in the GB region, the GB curvature value is modeled numerically. An experimental data on break-away effect on individual GB in aluminum and zinc are presented.

A qua n tative theory of diffusional impurity drag by a migrating GB was first suggested in 1957 by K.Lucke and K.Detert [1]. On the Lucke-Detert (L-D) theory a a migrating planar GB is a potential well for an impurity, owing to which the impurity gets adsorbed on it. If the GB motion is limited by the impurity – atom diffusion, the mobility of such GB:

$$m_L = \frac{D_o \exp(-Q/kT)}{\Gamma kT} = \frac{D_o \exp[-(U_o+Q)/kT]}{2\lambda C_o kT} \qquad (1)$$

here D_o and Q are preexponential factor and diffusion activation energy of the impurity, Γ is magnitude of of the impurity adsorption on the GB, U_o is mean energy of the impurity-boundary interaction (potential well depth), λ is the effective thickness of the GB, C_o is impurity concentration in the crystal bulk.

According to the L-D theory an impurity may move together with the GB at the velocity not exceeding the value

$$v^* = \frac{D_o \exp(-Q/kT)}{kT} \cdot \frac{U_o}{\lambda} \qquad (2)$$

where the U_o/λ ratio yields the estimation of a maximal force of the impurity atom-GB interaction. If the GB migration velocity is higher than v^*, the GB breaks away from the impurity. The mobility of the impurity-free GB m_F in this case must exceed appreciably

m_L.

The break-away of the migrating GB from the impurity, transiting to a new branch of motion is the kinetic phase transition whose intensive parameter is not a thermodynamic parameter (temperature, pressure, impurity concentration) but a kinetic one, i.e. the driving force of the GB migration.

The theory was further developed in the works by Cahn [2], Lucke and Stuwe [3] who look into account a diffusional spreading of the adsorption zone that followed the migrating GB. These theories suggest that impurity atoms not only "evaporate" from the GB with the temperature growth but, also, get "blown away" from it as the velocity increases. On the one hand, the faster the GB migration, the smaller number of atoms will keep back in a potential well, i.e. state. On the other hand, the smaller number of adsorbed atoms, the lower the dragging force and the higher the GB velocity are. Due to this positive feedback the GB loses in an avalanche fashion an impurity cloud. This, precisely, is the break-away effect, predicted by L-D.

Interest to this phenomenon is clear. First of all, this is a tool to study the GB - impurity. It enables one to reveal the impurity responsible for the GB drag, adsorption characteristics of this impurity on the GB, i.e. adsorption heat, number of adsorption sites, diffusion parameters of impurity atoms. But the main thing is that the break-away effect makes it possible to study properties of the GB free from the atmosphere of excessive adsorbed atoms. Herewith one can encounter unexpected effects and properties.

This program is most expedient to realize for individual GB of a certain crystallography, migrating under the action of an certain driving force, in alloys with a predetermined impurity composition.

Importantly, that all the theories of diffusional impurity drag consider a model GB all points of which are moving at identical normal rate. This is not the case in experiment. The break-away of a curved GB portion from an impurity is a more complicated process than that of a planar one. Below are given the basic results of the theory of the break-away of a curved GB, with

a moving GB half-loop taken as an example [6]. (Probably, the method to study the GB migration by means of a GB half-loop is most correct, safe and convenient at the present time - the constant driving force, the possibility to minimize side effects, including the disturbing influence of the external crystal surface and, finally, the possibility of accurate analytic representation of parameters of the process of the half-loop motion, including the rate of stationary motion as a function of the driving force if the dependence m(v) of a microscopic mobility of the GB portion on the velocity of its normal migration is known

$$V = \frac{2\sigma}{a} \int_0^1 \frac{m(\alpha V)d\alpha}{\sqrt{1-\alpha^2}} \qquad (3)$$

where M(V) is a mean half-loop mobility, and, the inverse problem, the possibility to recover the form of the dependence m(v) from the dependence of the velocity V on the driving force

$$m(V) = \frac{1}{\pi\sigma}\frac{d}{dv}\int_0^v \frac{a(V)V^2 dV}{\sqrt{v^2-V^2}} = \frac{1}{\pi\sigma v}\int_0^v \frac{a'(V)V+2a(V)}{\sqrt{v^2-V^2}} V^2 dV \qquad (4)$$

[6-9] (fig.1)).
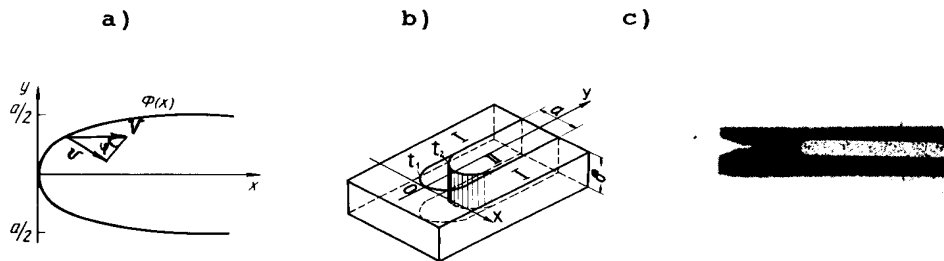
a)   b)   c)

Figure 1. Method of GB half-loop.

In the L-D approximation the GB mobility depends only on the temperature and velocity v. The surface tension of a GB σ varies

from point to point much weaker than the mobility, so one can assume σ = const [6]. Of all half-loop points its tip moves the fastest, its velocity equals the velocity V of the loop migration as a whole. If $V < v^*$ the GB will never break away from the impurity in none of its points (m = m_L = const). A half-loop whose velocity is greater than v^* will consist of GB portions both free (having broken away) from the impurity and moving together with the impurity. The GB portions, lying away from the half-loop tip, move slowly and therefore they don't break away from the impurity. As the moving half-loop is breaking away from the impurity, its shape changes (fig.2) and the migration velocity is determined by the dependence

$$v^* = V \sin\left(\frac{\pi}{2} \ \frac{V_F - V}{V_F - V_L}\right)$$ (5)

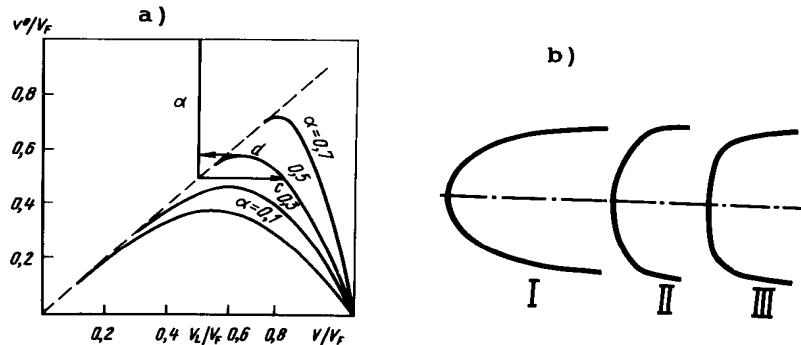where $V_F = \pi\sigma m_F/a$, $V_L = \pi\sigma m_L/a$.

Figure 2. Diagram for determination of the velocity of the half-loop stationary motion (a) and the shape of the GB half-loop during the impurity break-away process (b).

In fig.2 the dependence (5) is given schematically. One can see a hysteresis during the break-away (when v^*/V, decreasing, will reach the point b - the V_L/V_F value - a fraction of the impurity will break away from the loop tip, and the GB will acquire in a jump-like fashion a velocity, corresponding to the c-point) and "sticking" of the impurity (with an increase of v^*/V_F the half-loop velocity will after by the same curve to the d-point after

which it will become equal to V_L (impurity "sticking").

The GB break-away from the impurity is a vivid illustration of the principle of a maximal rate of a free energy decrease or the principle of an intermediate equilibrium [11,12]. (With present thermodynamic forces the system tends to reach the equilibrium in a shortest way, or: on the way to the equilibrium the system tends to occupy the state with a lowest free energy). The impurity adsorption on the GB is caused by the tendency to decrease the GB free energy; the impurity break-away increases the GB surface tension and increases drastically its mobility which facilitates a decrease of the free energy of the system.

The application of the macroscopic approach makes it possible to clearly interpret the problem in the L-D approximation [6]. The values of V, which are the solutions of eq (3), correspond to the extreme of the function $\Psi(V)$.

$$\Psi(V) = 2 \left[2\sigma V - a \int_0^V \frac{V dV}{M(V)} \right] \qquad (6)$$

Only the maxima of this function correspond to the stable stationary motion. The velocities, corresponding to the minimum of $\Psi(V)$, decrease with growing driving force, and these solutions are unstable (fig.3). Note, that at a linear dependence of the migration velocity on the driving force (M=const) the Ψ function is numerically equal to the free energy dissipation, which complies with Onsager's principle in thermodynamics of irreversible processes.
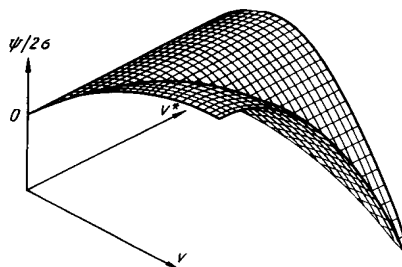

Figure 3. Overall view of the generalized dissipative function.

The next step was taken in the work [13]. In the framework of the continuum approximation (Lucke-Stuwe,Cahn) [3,4] a numerical method was used to analyze how much the process of break-away is affected by the form and value of the GB -impurity interaction potential, the GB curvature, differences of the impurity diffusion coefficient in the GB region from its bulk value. As shown in [13], neither the potential form nor the GB curvature affect, practically, the parameters of the diffusional impurity drag and GB break-away from the impurity (fig.4). As the impurity - GB interaction energy U_0 grows, the value of the driving force at which , the break-away takes place increases (naturally!). Interestingly, that with small value of U_0 the break-away in the form of an abrupt jump is transformed to a smooth bending on the curve. Noteworthy is the dependence of the break-away parameters on the GB to bulk diffusion coefficient D_b/D_v. (In [13] D_b is the function of the coordinate respect to the normal to the boundary $D_b = D_b(x)$). An increase of D_b/D_v shifts the break-away point forwards the region of high driving forces. which is physically explainable: mobile impurity atoms go on moving with the boundary at large GB velocities, corresponding to large driving forces. Of interest, however, is the following fact. Having compared the calculation with the experiment, the authors of [13] found that already with $D_b/D_v \simeq 100$ the break-away temperature exceeds that of the sample melting (aluminum in this case), and the calculated and experimental break-away temperatures coincide at $D_b/D_v \simeq 10$. In the opinion of the authors of [13] this gives evidence to the fact that D_v cannot be similarized with the coefficient of diffusion along the GB (at considered temperatures the GB diffusion coefficient in the sample material, determined by a standard technique, $D_b \gtrless 10^5 - 10^6 D_v$).
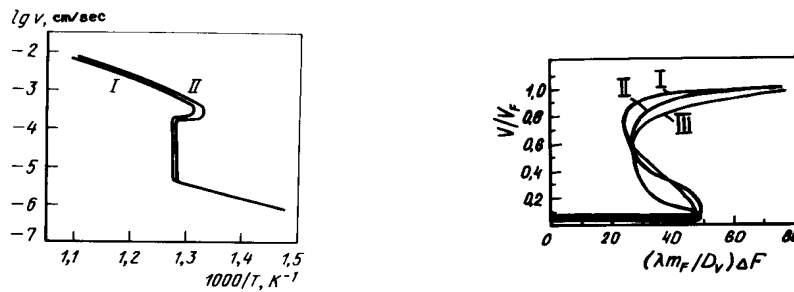
Figure 4. Dependence of the velocity : a) of a planar (I) and curved (II) GB on the temperature; b) on the shape on the GB - impurity interaction potential (I - triangular; II - trapezoidal; III - Gaussian).

Experimentally the effect of the break-away of the moving GB from the impurity was observed and studied on individual tilt GB_<111> in gold [14] and aluminum [15-17], <10$\bar{1}$0> and <11$\bar{2}$0> in zinc [18-20] (fig.5). Fig.6 shows the temperature dependencies of the mobility of a tilt GB <111>,φ=36.5°$\pm$0.5° in high-purity aluminum samples [16](I-V) specially doped with iron in concentrations, though rather low but significantly exceeding the concentration of any other dissolved elements (tab). A characteristic feature of the considered dependencies is a drastic change of the GB velocity in a narrow temperature range. Above and below the break-away region the GB velocity is temperature dependent in the usual activation manner.
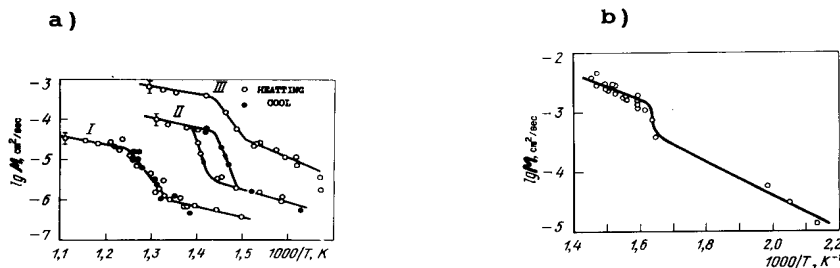
a)   b)

Figure 5. Temperature dependencies of the mobility M of tilt GB <111> (φ=38°) in aluminum (a) and (10$\bar{1}$0) (φ=30°) in zinc (b).
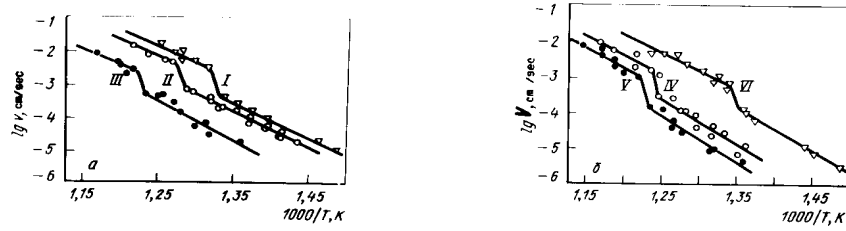
Figure 6. Temperature dependence of the velocity of a tilt GB <111> ($\varphi=36.5°\pm0.5°$) in iron-doped aluminum samples (Table).

ADSORPTION OF THE IMPURITIES ON THE GRAIN BOUNDARIES

Metal	Tilt GB	Braking impurity	$c, 10^{-5}\%$ (at.)	U_o, kJ/mol	z, cm^{-2}	Γ, Γ at/cm^2
Al	<111> $\varphi=38°$	Fe	2	1 0	$2.3.10^{14}$	–
			1	1.4	$7.0.10^{13}$	–
			1	1.4	$2.4.10^{14}$	–
Zn	<11$\bar2$0> $\varphi=34°$	Al	3	1.9	$5.9.10^{13}$	$1.5.10^{10}$
	<11$\bar2$0> $\varphi=88°$		3	2.0	$8.8.10^{13}$	$1.5.10^{10}$
	<10$\bar1$0> $\varphi=30°$		3	1.0	$1.4.10^{15}$	$1.3.10^{10}$
Al	<111> $\varphi=36.5°$	Fe (sample I)	7*	0.9	$1.0.10^{14}$	$1.7.10^{8}$
		(sample II)	7*	0.7	$1.4.10^{14}$	$6.0.10^{8}$
		(sample III)	8	0.7	$1.4.10^{14}$	$6.2.10^{8}$
		(sample IV)	1.5	0.7	$1.4.10^{14}$	$8.9.10^{8}$
Al	<111> $\varphi=36.5°$	Fe (sample V)	1.6	0.7	$1.1.10^{14}$	$11.3.10^{8}$
		(sample V)	1.65	0.8	$1.3.10^{14}$	$15.9.10^{8}$
	<111> $\varphi=46.5°$		8	0.7	$1.4.10^{14}$	$6.1.10^{8}$
				1.6	$4.9.10^{12}$	$2.1.10^{8}$
	<111> $\varphi=46.5°$		6	0.8	$1.7.10^{14}$	$7.4.10^{8}$
				1.8	$4.2.10^{12}$	$2.6.10^{8}$
			5	0.8	$1.3.10^{14}$	$5.6.10^{8}$
				1.8	$3.8.10^{12}$	$1.9.10^{8}$

* $\Delta F_I/\Delta F_{II} = 1.6$.

A considerable experimental material has been accumulated be the present time. The effect was observed on special and close to special GB; no effect was found on general GB and in materials with high impurity content. It was been noted afore that the break-away effect is a fine tool to study the adsorption properties of GB. This is supported by the data of table, fig.6 — the temperature dependence of the iron atoms adsorption on an individual tilt GB <111>, $\varphi=36.5^{\circ}$, and by the results of study of the <111> special tilt GB migration, $\varphi=46.8^{\circ}$ (inverse density of coincidence sites $\Sigma=19$) in iron-doped aluminum samples [17].Temperature dependencies of the mobility of this GB in doped samples exhibits a double sequential jump, followed by a drastic alteration of the migration activation energy (fig.8). An analysis of the obtained data has shown that the observed mobility jumps are related to the break-away of the migrating GB from adsorbed iron atoms, and the sequence of the break-away is attributed to the existence in said special GB of adsorption centers of two types, drastically different in the interaction energy of an impurity atom with the GB ($U_{01}=2.9\pm0.2$ kcal/mol, $U_{02}= 7.1\pm 0.4$ kcal/mol), the number of these centers being $Z_{1}=(1.5\pm0.2)10^{14}$cm^{-2} and $Z_{2}=(4.4\pm0.3)10^{12}$cm^{-2}. It appeared [17] that Z, correlates with an averaged (with respect to deviation angles from symmetric position) surface density of coincidence sites $d=1.8\cdot10^{14}$cm^{-2}. Active centers of type I may be interpreted as most distorted regions between coincidence sites. Centers of type II are supposed to be places on GB dislocations [17]. It should be noted that the data of the migration experiments quantitatively supported the known anomaly of the iron-atom diffusion in aluminum where, from the data of several authors, one can observe two drastically different groups of diffusion characteristics. Most common is the opinion about the relationship of this anomaly with diffusion in detective crystal regions.

The hypothesis, that the abrupt change of the migration velocity is connected with the phase transition discussed (GB detachment from impurity) may be supported by the following factors: the constant value of the calculated interaction energy U_{0} and the number of adsorption sites Z (in the bars of

experimental error) for the samples with fixed type of the GB but the different impurity content (Table); the correct shift of the detachment temperature , when increasing concentration of impurity and driving force of migration. On fig.7 one can see the temperature dependence of the tilt <111>, 36.5°, GB mobility for the aluminum samples (I & II) with the equal iron content but different migration driving force ($\Delta F_I/\Delta F_{II}$ = 1.6), the absolute value of the driving force in this experiment being small ($\Delta F \simeq 10^{-6}$ kT). Velocities and temperature intervals of the effect differ for two samples while the mobilities at the low - and high-temperature regions coincide with each other. It is the confirmation of the fact, that the driving force namely determines the temperature interval of the effect . The quantitative agreement obtained also confirms the nature of the effect.
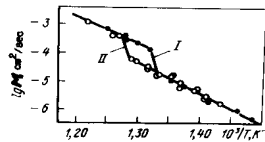

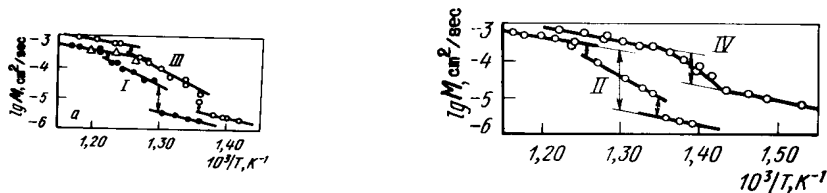Figure 7. Temperature dependencies of the mobility of a tilt GB <111> (φ=36.5°) for samples I and II (Table).

Figure 8. Temperature dependencies of the mobility of a special tilt GB <111> (φ=46.5° $\pm$0.5°) in iron-doped aluminum samples.

Of considerable interest is an analysis of the number of adsorption centers in different boundaries, determined as a result of the break-away effect data treatment, For different tilt GB Z changes from $\sim 5 \cdot 10^{13} cm^{-2}$ (zinc, tilt GB $<11\bar{2}0>$, $\varphi = 56°$), to $\sim 10^{15} cm^{-2}$ (zinc, tilt GB $<10\bar{1}0>$, $\varphi = 30°$). This difference in the adsorption ability gives rise to a number of effects. So, at the same concentration of a soluble impurity on the tilt GB $<10\bar{1}0>$ and $<11\bar{2}0>$, in zinc one can observe principally different orientation dependencies - the difference in the adsorption capacity and the adsorption heat leads to the fact that on the GB $<10\bar{1}0>$ the adsorption saturation ensues earlier than on the tilt GB $<11\bar{2}0>$ [21,22]. Therefore, at the same impurity concentration the properties of special and general tilt GB $<10\bar{1}0>$ are levelled, and those of $<11\bar{2}0>$ are different.

Figure 9. Temperature dependencies of the mobility of tilt GB $<11\bar{2}0>$ in zinc.

The second effect is associated with the existence of GB with low adsorption ability. This is the effect of athermal (non-activated)) migration of GB. It was experimentally observed on special and close to special tilt GB $<11\bar{2}0>$ [19,20]. Fig. 9 shows the temperature dependencies of mobility of the GB which exhibited the effect in question. The course of the dependence M(T) is characteristic of the afore considered effect of break-away of a migrating boundary from the adsorbed impurity. An important new feature is that after the break-away from the impurity atmosphere the GB velocity is temperature independent. Physically, this phenomenon is clear in pure material, where the

GB is not a marker in the material sense but is a kind of energetic disturbance, its motion can occur by way of propagation of this disturbance, i.e. analogous to the wave motion, conservative motion of dislocations in pure material.

This effect was phenomenologically described in [20,21] in the framework of the theory of transitional state and Zener elastic model of atomic transitions. In this model free activation energy is the work of effective deformation of the matrix or the work of critical displacement of an atom or a group of atoms. The expression for the GB velocity is

$$V = \beta b\nu \frac{\Delta F}{kT} \exp\left(\frac{S^*}{k}\right) \exp\left(-\frac{E}{kT}\right) = M_0 \frac{\Delta F}{kT} \exp\left(-\frac{E}{kT}\right) \qquad (7)$$

where β is the parameter, depending on the type of atomic transition during the GB migration: $\beta=n$ for a group collective transition (at an elementary act of the GB displacement a group of n noninteracting with each other atoms transits from grain into grain); $\beta=1/n$ – for a group cooperative transition (a group of n atoms consistently displaces, driving one atom through the GB; during this event the matrix deformation is produced by all n atoms); finally, for the migration mechanism by way of individual atomic transitions $\beta=1$, b is the lattice parameter, ν is the frequency of atomic oscillations, S and E are activation entropy and energy, respectively. It follows from (7) that the dependence $E = f(\ln M_0)$ is a straight line, the same for all transition mechanisms. Fig.10(a) shows this dependence schematically, fig.10(b) shows the dependence $E = f(\ln M_0)$ for tilt GB $<11\bar{2}0>$ in zinc. The points, corresponding to nonactivated regions of the motion fit the straight line as well.
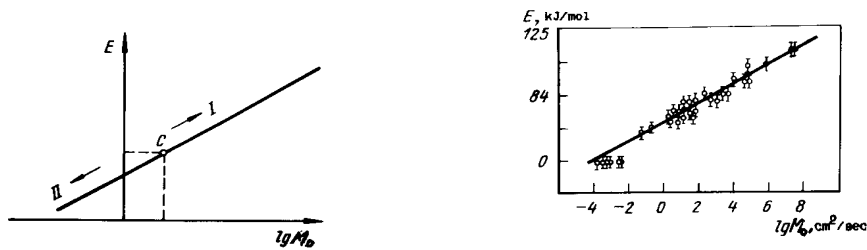
Figure 10. Dependence of the activation energy E on the logarithm of the preexponential multiplier : a) schematic; b) experiment (tilt GB <11$\bar{2}$0>,zinc).

The non-activated motion of GB was observed in molecular dynamics studies of the GB migration [22].

The influence of a GB-dragging impurity on the effect of the nonactivated motion is manifested in two ways. First, an increase of zinc purity leads to an increase of the number of the GB on which the effect of the non-activated motion is manifested. Second, the impurity decreases the GB mobility on the non-activated region (fig.11). This fact cannot be explained on the base of the theory of diffusional impurity drag since (in our presentation) on the athermal region the GBis moving without the adsorbed (without the excessive in Gibb's sense) impurity atoms. The authors of [23] proposed a model of the phenomenon where the impurity atoms in the crystal bulk act as pinning in the non-activated region is given as

$$V \overset{\sim}{=} (M\Delta F/2)\left[1+ \sqrt{1- \frac{8C_0 D(kT)^{-1}U_0\lambda^{-1}M}{(\Delta FM)^2}}\right] \qquad (8)$$

Here C_0 is the number of impurity atoms in 1 cm^3, D is the coefficient of the impurity diffusion. According to (8) an impurity may decrease the velocity in the nonactivated region by not less than twice, that agrees with experiment in the order of magnitude (fig.11).
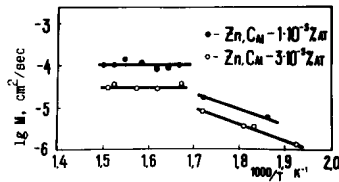
Figure 11. Temperature dependence of a tilt GB <11$\bar{2}$0>, φ = 50° in zinc of different purity: $\bullet$ - 10^{-5}% at. Al; $\circ$ - 3.10^{-5}% at. Al.

Experiments carried out for a tilt GB <11$\bar{2}$0>, φ=86° at a constant driving force of the migration process (by a method of a GB half-loop) showed a strong dependence of the mobility on the non-activated region on the GB orientation in a bicrystal (inclination) (fig.12) [21]. The mobility maximum approximately coincides with the plane (10$\bar{1}$2) of a middle grain. It would be interesting to analyze (like it is done at martensitic transformations) what defects may govern the non-activated motion of a GB. As the driving force is increased, the non-activated motion of first point, then linear and finally the whole GB becomes possible. At martensitic transformations the latter case is realized since the driving forces are great there. In our case the driving forces are smaller by several orders of magnitude, and the velocity of the non-activated motion is comparatively low. This suggests that, e.g., linear defects on the GB can move in a non-activated fashion. Thus moving, a linear GB defect ($h \simeq 10^{-8}$cm in height), perpendicular to the GB plane, will "sweep off" the cylindric GB portion at the velocity of sound ($c \approx 3 \cdot 10^5$cm/s). The GB mobility is $M = ch/\pi \simeq 10^{-3}$ cm/s, that is close to a maximal mobility in the order of magnitude in our experiments.
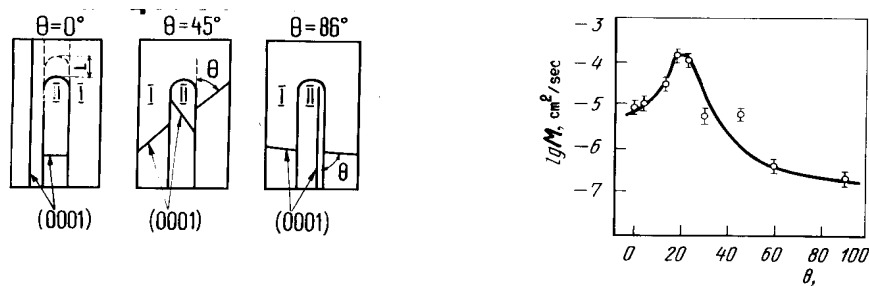
Figure 12. Bicrystals with different orientation (inclination) θ of a tilt GB $<11\bar{2}0>$, $\varphi = 86°$, and the dependence of the mobility om θ on the non-activated region.

The work [24] gives a general theory of stationary motion of a GB under the action of the intrinsic surface tension. It is shown in [24] that in the absence of a clear dependence of the reduced mobility of a GB element on the velocity of a regular motion, i.e. in the case of a linear relationship between the velocity and driving force the dependence of the stationary motion velocity on the half-loop orientation is governed by the difference of mobilities of straight (immobile!) GB portions. In crystals whose lattice possesses the inversion symmetry the half-loop velocity may depend on its orientation with respect to crystallographic directions. The question is: what is the observed dependence of the mobility on the orientation in the crystal related to (fig.12) — the absence of the inversion symmetry or the non-linearity of the dependence of the velocity on the driving force? The answer is the eq (10):

$$\frac{dV}{d\alpha} = \frac{M_L(\alpha + \pi/2) - M_L(\alpha - \pi/2) + \Delta M(\varphi_1^*) - \Delta M(\varphi_2^*)}{\alpha - [(v^*/V)/\sqrt{V^2+v^{*2}}][\Delta M(\varphi_1^*) + \Delta M(\varphi_2^*)]} \qquad (10)$$

where $\Delta M(\varphi) = M_F(\varphi) - M_L(\varphi)$; $\varphi_{1,2}^* = \alpha \pm arc\ cos(v^*/V)$, α is the angle between a certain fixed direction in the crystal and the direction of the half-loop motion (straight regions).

One can see that the orientation dependence of the half-loop velocity can actually be governed both by the absence of the inversion symmetry and the non-linearity of the dependence of the velocity on the driving force. But in the concrete experimental conditions [23] ($M_F/M_L \gg 1$, $V/v^* \gg 1$)

$$\frac{dV}{d\alpha} = \frac{\left[M_F \left(\alpha + \pi/2 \right) - M_L \left(\alpha + \pi/2 \right) \right]}{\alpha} \tag{11}$$

So, the orientation dependence of the velocity in this case is governed, seemingly, by the difference in the mobilities of the impurity-free GB elements, turned by 180^0, whereas the role of non-linearity in this experiments is small.

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