CONCLUSIONS

1. The results of the calculations provide no basis for conclusions as to the best of the modifications used.

2. Calculations must allow for asymmetry of the curves of solid phase separation.

3. Sytems Ni–Cr, Ni–Ru have not received sufficient experimental investigation. It is therefore not clear whether the differences are due to the inadequacies of the precise models of the calculation or to experimental errors.

4. Parameters B^*, E^* and A^* are not sufficiently well defined. The complete parameters B^*+e_1; E^*+e_1, A^*+e_1, are more convincing, and for most systems they prove to be similar to one another in all three modifications.

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DEPENDENCE OF THE RATE OF NON-ACTIVATED MOTION OF A GRAIN BOUNDARY ON ITS ORIENTATION*

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The orientation dependence of the rate of unactivated motion of a tilt boundary (axis $\langle 11\bar{2}0\rangle$, misalignment 86°) is investigated in zinc. That velocity and its orientation dependence is explained by analogy with the motion of a phase boundary during martensitic transitions and the hypothesis of best coincidence orientations.

The phenomenon of non-activated motion of large-angle grain boundaries has been disclosed in [1] (on special tilt boundaries with axis $\langle 11\bar{2}0\rangle$ in zinc of purity 99·995 at.%). Since the effect has been observed on singular boundaries and is associated with the possibility of orientation rearrangement

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of atoms on either side of a boundary, it is probably interesting to study the influence of crystallographic factors on that motion. One such factor could be that of how a boundary is oriented in a bicrystal with a certain angle of misalignment.

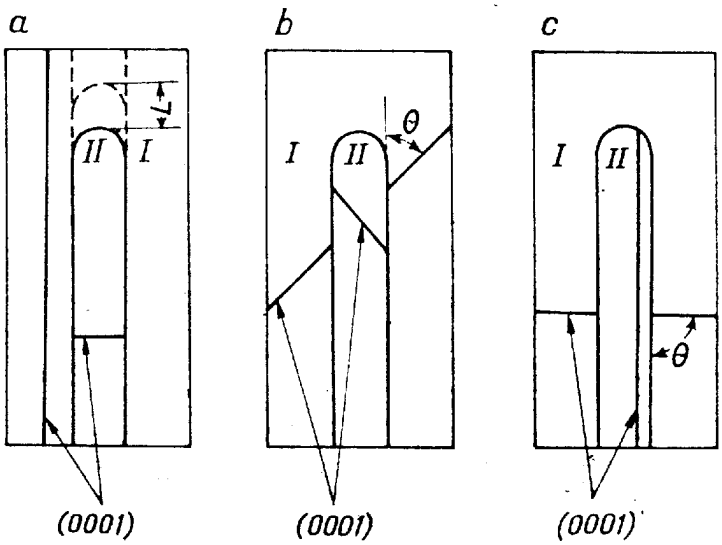

FIG. 1. Biocrystals with different orientations of the grain boundary; tilt boundary $\langle 11\bar{2}0\rangle$, $\varphi = 86°$, Zn: $a - \theta = 0$; $b - 45$; $c - 86°$.

The purpose here is to see how the mobility of a boundary during non-activated motion is influenced by its orientation in a bicrystal, the misalignment of the two halves of that bicrystal remaining unchanged.

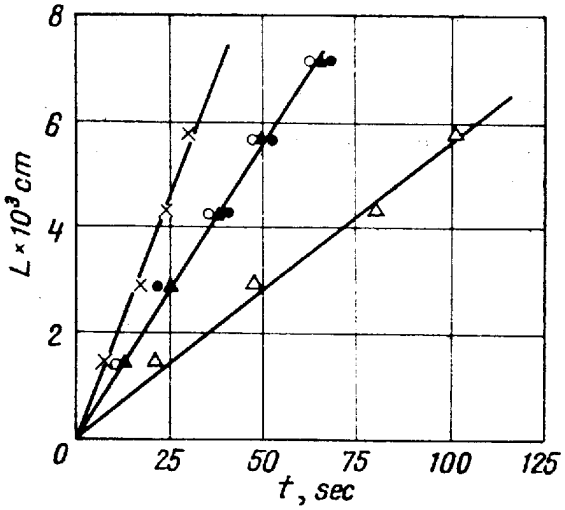

FIG. 2. Dependence of boundary position L on time t; tilt boundary $\langle 11\bar{2}0\rangle$, $\varphi = 86°$, $\theta = 4°$, Zn: △ – $T = 608$; ● – 650; ▲ – 661; ● – 672; × – 689 K.

The experiments have been conducted in the method of the migration of a single boundary where the driving force of the process is constant [2]. That constancy was maintained within 1 %. Using that procedure specimens were produced with different boundary orientations but constant misalignment of the grains. The angle of orientation θ of the boundary was found as the angle between plane (0001) in grain I and the plane of the boundary (Fig. 1).

All the angular characteristics of the specimens were measured with an optical method using splinters on planes (0001). The angle were measured within 20′.

The angle of misalignment of the two halves of the bicrystal deviated by not more than ±30′. The other angular parameters were preserved with the same degree of accuracy, that is, perpendicularity of the boundary and axes ⟨11$\bar{2}$0⟩ of the two parts of the bicrystal to the surface of the specimen. To study the migration we used an optical microscope with a high-temperature attachment, in polarized light. The boundary position was registered within 3×10^{-4} cm. The time was measured within 0·1 sec and the temperature deviation was not more than ±0·5°C from the given point. The investigations were performed on zinc 99·995 at.%.

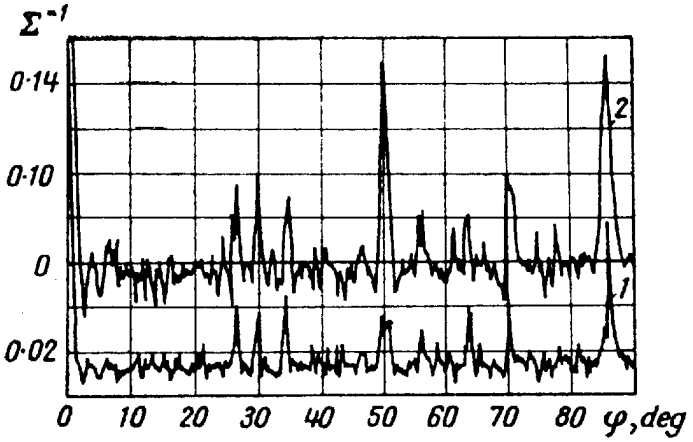

FIG. 3. Dependence of number of coincident sites on misorientation for alignment with ⟨11$\bar{2}$0⟩, Zn: 1 – ε=0·07 a; 2 – 0·15 a.

Typical curves of the boundary position L vs. time t are shown in Fig. 2. The error in determination of the mobility A was thus not more than 10%, and the activation energy of migration – 1 k·cal/g·at.

Obviously it is best to study the orientation dependence of the mobility on a boundary where the non-activated motion is most marked. It has been found that in specimens with a given impurity concentration the effect is only observed on singular boundaries, so the best of those had to be selected. This was done by calculating the dependence of the fraction of coincidence sites $\sum^{-1}$ on the angle of misorientation φ round axis ⟨11$\bar{2}$0⟩ in Zn in the model of a short-range coincidence lattice [3] because perfect site coincidence is only possible for an h.c.p. lattice with rotation round axis (0001), the c/a ratio not being rational in real lattices. The program was designed to calculate the dependence $\sum^{-1} = \sum^{-1}(\varphi)$ for different degrees of non-coincidence of sites ε

$$\varepsilon = |\mathbf{R}_i^{(1)} - \mathbf{R}_k^{(2)}|, \tag{1}$$

where $\mathbf{R}_k^{(1)}$ and $\mathbf{R}_k^{(2)}$ are the radial vectors of the i-th atom of the 1st crystal and k-th of the 2nd crystal respectively. In size, the cell calculated for each of the grains was 1764 at. The calculation was performed for ε=0·05 a, 0·07 a, 0·10 a and 0·15 a. Figure 3 gives the results for ε=0·15 and 0·07 a. Obviously, when $\varepsilon_1 > \varepsilon_2$

$$\sum^{-1}(\varphi_0, \varepsilon_1) > \sum^{-1}(\varphi_0, \varepsilon_2), \tag{2}$$

because the number of coincident sites grows with ε; and so does the background, which consists of randomly coincident sites. From those results we selected a tilt boundary ⟨11$\bar{2}$0⟩ with misalignment of 86° because it corresponds to the maximum of $\sum^{-1}$.

Typical temperatures of the boundary mobility are given in Figs. 4*a–b*. In the low-temperature range it varies exponentially with the value T^{-1}, which indicates activation type of motion. Then, in

quite a narrow temperature range, there is a sudden increase of mobility (by 1–2 orders of magnitude) after which it remains constant up to the melting point. We have observed that kind of behaviour previously, where we interpreted it as being due to the detachment of a moving boundary from an atmosphere of adsorbed impurities [4]. This is supported by the following: detachment occurs on singular boundaries in high-purity crystals, starting from lower and lower temperatures as the driving force grows. After detachment from the adsorbed impurity the boundary migration becomes non-activated.

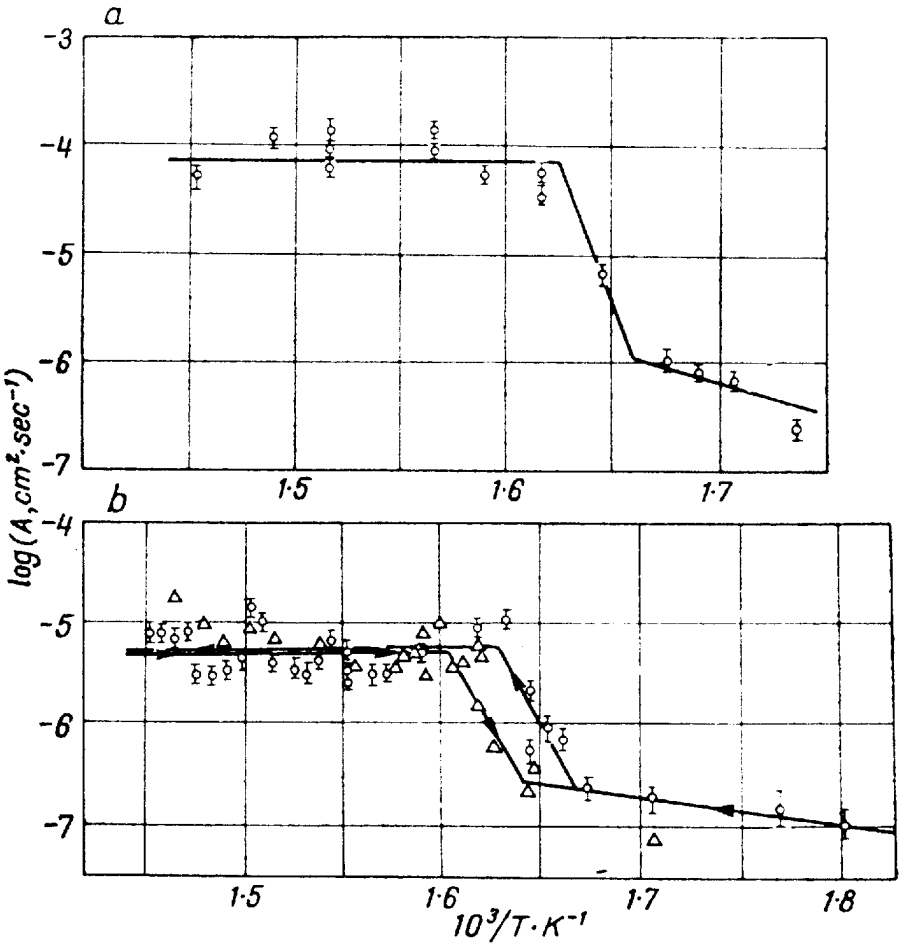

FIG. 4. Temperature dependence of grain boundary mobility; tilt boundary $\langle 11\bar{2}0\rangle$: $\varphi = 86°$; $\theta = 22$ (*a*); $\varphi = 4°$ (*b*), Zn.

That kind of temperature dependence is presumably associated with a mechanism of boundary migration very similar to that of diffusionless martensitic transition. In that case the boundary motion will depend on the concerted migration of groups of n atoms each of which covers a distance less than the interatomic spacing. Perfect boundary, low concentration of impurity atoms, the fact that exactly the same phase is on either side of the boundary, – those are the conditions of that mechanism, known as the group cooperative mechanism, and which is also observed in our case on the boundary of grains with a high density of coincident sites in a pure material, 99·995% Zn.

The authors have analyzed that kind of motion in the elastic model and theory of absolute reaction rates. In our case, the allowance for cooperative motion in that approximation gives the following formula for the velocity of boundary migration

$$v = bv \frac{\Delta F_1}{kT} \exp\left[\frac{\gamma E_1^*}{nk}\right] \exp\left(-\frac{E_1^*}{nkT}\right). \tag{3}$$

Here b is the atomic distance, ν – the frequency of atomic vibrations, ΔF_1 – the driving force for the transition of one atom, E_1^* – the activation energy of the unit process, $\gamma = \frac{d(\mu/\mu_0)}{dT}$, where μ and μ_0 are elastic moduli at the experimental temperature and 0 K respectively.

In this model, when $n \simeq 10$, which is the same order of magnitude as the number of atoms in a boundary structure unit, the activation energy is of comparable order of magnitude with the kT (at the experimental temperature). Macroscopically, this is seen in the non-activated type of motion.

Figure 5 gives our experimentally determined curves of the mobility A of a tilt boundary $\langle 11\bar{2}0\rangle$ with angle of rotation 86° on the non-activated intercept as a function of orientation θ. We investigated nine specimens in the entire range of angle θ ($\theta = 0$, 4, 14, 19, 22, 30, 45, 60 and 90°). The angle of orientation θ was imparted in the process of growing a specimen. As we can see, the boundary mobility varies non-monotonically with θ but the amplitude is quite large $\frac{A(\theta=20°)}{A(\theta=90°)} \simeq 10^3$. Maximum mobility corresponds approximately to plane (1012) of the central grain (Fig. 6). This fact is interesting because, as shown in particular by our calculations, the more densely coincident sites are distributed on plane $(10\bar{1}1)$. In the model of structure units, however, the boundary in plane $(10\bar{1}2)$ possesses the least of such units [3].

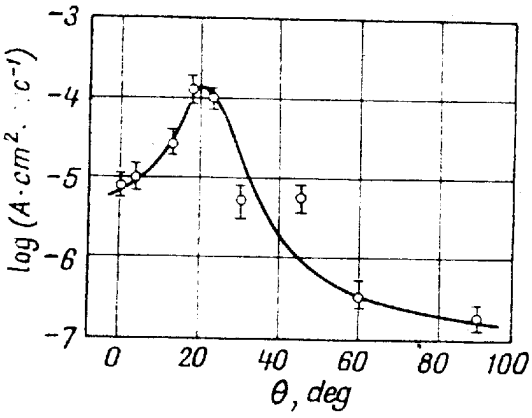

FIG. 5

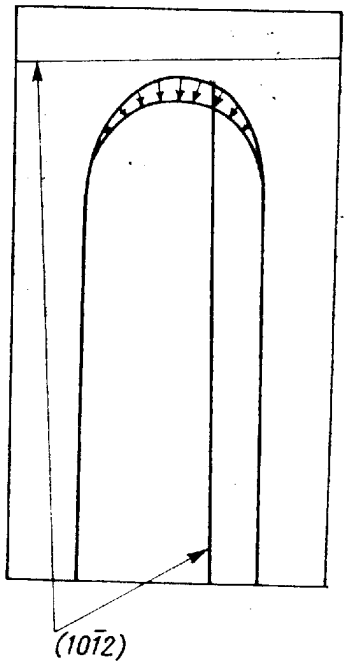

FIG. 6

FIG. 5. Dependence of grain boundary motion on the non-activated segment on the angle of misalignment; tilt boundary $\langle 11\bar{2}0\rangle$, $\varphi = 86°$, Zn.

FIG. 6. Diagram of normal component of boundary velocity.

$(10\bar{1}2)$ is the twinning plane in Zn [5]. From this viewpoint the maximum on the curve of A vs. θ (see Fig. 5) can be explained as follows: in our method the distorted boundary segment moves as a whole so the boundary velocity component parallel with its flat segments must be exactly the same for all points of the half-loop. Nevertheless, the component normal to the boundary varies from zero at the point where the bent half-loop is tangent with the immobile segment, to a maximum value at the tip

of the half-loop (Fig. 6). And, once again, this component is assumed to be responsible for all the observable effects. The tip of the half-loop lies in plane $(10\bar{1}2)$ of the central grain at $\theta = 20°$. This may mean that there is a connection between the process of twinning and of non-activated migration.

It follows from the above that the more perfect a boundary at the tip, the less is its absorptive capacity and the greater the mobility of the cylindrical part on the non-activated segment. Now let us analyze this phenomenon of non-activated boundary motion from the viewpoint of the motion of phase boundaries during martensitic transition [6]. If the matching of the lattices is good the potential barriers to boundary motion are lower and, the barrier on the boundary will be lower for a point* than a line defect†, the latter barrier in its turn being lower than for the boundary as a whole. As the driving force grows, non-activated motion becomes possible, first of point then of line defects and, finally, of the entire boundary at the velocity of sound in the crystal.

It is usually the latter case which is observed in martensitic transitions, because the driving forces are so enormous, much greater than can ever be reached for grain boundaries. The velocity of their non-activated motion is quite small. That means, for example, that line defects on a boundary can move without thermal activation. Let us evaluate the boundary mobility in that mechanism. Moving without activation a line defect‡ of a boundary of height $h \simeq 10^{-8}$ cm, perpendicular to the plane of the specimen, will wipe the cylindrical part of the boundary, like a windscreen wiper, at the speed of sound (3×10^5 cm/sec). The mobility of the boundary

$$A \simeq \frac{ch}{\pi} \simeq 10^{-3} \text{ cm}^2/\text{sec} \tag{4}$$

In order of magnitude this approximates to the maximum mobility obtained in our experiments. A would have a value eight orders of magnitude greater for the non-activated motion of a boundary as a whole. If point defects migrate without activation the mobility would be 10^{-11} cm^2/sec, which is much less than that measured experimentally.

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* A break on a step.

† Steps on a boundary.

‡ For instance, it could be a grain boundary dislocation and the point defect, a kink on it.