Dynamic strain aging in materials with a high Peierls relief: competition of diffusion and dragging impurities

B V Petukhov
Shubnikov Institute of Crystallography, Russian Academy of Sciences, Leninskii pr. 59, Moscow, 119333 Russia
petukhov@ns.crys.ras.ru

Abstract. A model of the dynamic interaction of dislocations with the impurity subsystem of crystals that have high Peierls barriers has been developed. It is justified that the impurity kinetics during atmosphere formation includes two stages. The initial stage leads to a negative strain rate and positive temperature dependence of the yield stress of the material in some range.

1. Introduction
The effect of impurities on the dislocation dynamics significantly modifies the mechanical properties of crystalline materials. When the dislocation and impurity mobilities are comparable, plastic flow instability often arises (the Portevin–Le Chatelier effect [1]). The dynamic aging of dislocations is also considered as a possible reason for the temperature and strain rate anomalies of the yield stress of materials ([2,3], etc.). To date, the dynamic interaction of impurities with dislocations has been well studied for fcc crystals (see for reviews [4,5]) and much less for bcc metals, semiconductors, ceramics, and other materials in which dislocation motion is controlled by the Peierls barriers. The key problem of the theory of dynamic strain aging of materials is the variation of the impurity content in dislocation lines. The consideration of this problem in literature is too simplified; in many cases, the kinetic law is just postulated as a simple extrapolation between the initial diffusion power-law Cottrell-Bilby kinetics of impurity segregation in a dislocation line and the final approximation to equilibrium [6]. However, this approach may underestimate the impurity content at dislocations, because it does not take into account the impurity dragging. To understand this phenomenon better, it would be useful not to postulate but to derive a kinetic law from the underlying physical mechanisms. This is the purpose of the present study.

1. Model of short-range dislocation-impurities interaction
At different velocities of dislocations, different spatial scales of their interaction with impurities manifest themselves. We are interested in the case of sufficiently fast motion, when distances of the order of few lattice parameters around a dislocation are significant. The dislocation motion on the atomic scale (between valleys of the periodic crystal lattice) occurs, as is known, via thermally activated jumps [1,2]. A sharp change of the dislocation position in the slip plane leads to redistribution of the impurity atmosphere in each step, the redistribution kinetics depends on the structure of the potential profile for impurity migration in the vicinity of dislocation core. The simplest one-dimensional shape of such relief is schematically shown in figure 1.
Far from a dislocation, the migration relief is periodic and the time $\tau_0$ of impurity displacement by the lattice parameter is unperturbed. In the vicinity of dislocation core, the profile is distorted by the interaction in such a way that there is a deep minimum corresponding to the most energetically favorable impurity position with respect to the dislocation, which is indicated by the letter $d$ in figure 1. The attraction to this position reduces barrier $E$ for impurity transition into it and decreases the time of the corresponding thermally activated jump $\tau=\tau_0\exp(E/kT)$ in comparison with the time of reverse transition, $\tau_1=\tau_0\exp(E_1/kT)$, or the time of migration far from the core, $\tau_0=\tau_0\exp(E_0/kT)$, thus, $\tau<\tau_0<\tau_1$. The meaning of the activation energies $E_1$ and $E=E_1-\Delta E$ is explained in figure 1.

We focus on calculating the occupancy of the state $d$, which is a trap for impurities, the other states in the simplest approximation will be considered as weekly perturbed and interpreted as some reservoir with a constant concentration $c_0$. An exception is the (+) and (−) states (adjacent to $d$ in the slip plane) because, due to the dislocation motion with possible entrainment of impurities, the impurity concentration is significantly redistributed between these states.

Let us analyze the evolution of the impurity concentration in the dislocation core $c_d$. We will also introduce the designations $c_+$ and $c_-$ for the impurity concentrations in the (+) and (−) states. We can write the equations for impurity redistribution between these states and the crystal bulk during the waiting time $t_a$ for jump to the next valley, when the dislocation is at rest in one of the potential valleys:

$$\frac{dc_+}{dt} = (c_++c_-)(1-c_d)/\tau - c_+(2-c_+-c_-)/\tau_1,$$

$$\frac{dc_-}{dt} = -c_+(1-c_d)/\tau + c_d(1-c_+)/\tau_1 - c_+(1-c_+)/\tau_0 + c_0(1-c_-)/\tau_0. \tag{2}$$

The first terms on the right-hand sides of these equations describe the flux of impurities from the adjacent (+) and (−) states to the core ($d$) per unit time, the second terms describe the reverse flux. The third and fourth terms on the right-hand side of (2) describe the exchange by impurities between the (+) and (−) states and the crystal bulk. Equations (1) and (2) take into account that transitions may occur only to unoccupied states: for example, the transition frequency to the state $d$ is proportional to the probability $1-c_d$ that this site is free, etc.

![Figure 1. Schematic diagram of the migration relief of impurities near a dislocation core. The states directly in the core (d) and the neighboring states in the slip planes (+) and (−) are selected, with indication of the impurity transition times between these states and the crystal bulk.](image1)

![Figure 2. Variation of impurity content at an initially fresh dislocation in course of sequential jumps. The dashed line marks the steady amplitude value of impurity content established at $t\to\infty$ ($c_0=0.1$, $t_a=10\tau$).](image2)
Due to the large difference in the times of impurity transitions to the dislocation core ($\tau$) and the neighboring lattice sites ($\tau_1$ and $\tau_0$), the evolution of the impurity content occurs in two stages with significantly different durations. During a time of about $\tau$, only the fastest transition of impurities from the nearest states (±) to the core (d) occurs, without the participation of more distant impurities. And only then, for a time of about $\tau_0$, exchange with impurities from the reservoir occurs and the equilibrium concentration is established. The presence of the pronounced initial stage, describing the behavior of far from equilibrium impurity content, results in a number of peculiar effects, which are considered below.

3. Entrainment of impurities at steady dislocation motion

On the microscopic level, the dislocation motion over the Peierls barriers occurs via successive thermally activated jumps by a lattice period $a$ with jump waiting times $t_a$, thus, the average dislocation velocity is $V_d = a/t_a$. The impurities in the dislocation core behave differently, depending on the migration barrier height. At a sufficiently high binding energy $\Delta E$, as opposed to the barrier height $E$, impurities are predominantly entrained by the dislocation to the next potential valley. At the reverse relation ($\Delta E < E$), impurities are predominantly dropped away the dislocation and remain in the initial valley. This condition gives an approximate quantitative criterion for distinguishing by convention high- and low-mobile impurities. A complete analysis of model predictions is given in [7]. Let us shortly describe the behavior of low-mobile impurities ($\Delta E < E$).

Using equations (1), (2), one can easily calculate kinetics of dynamic aging of a dislocation, as is shown in figure 2. Accumulation of impurities due to the dragging is clearly seen, which illustrates the necessity to modify the Louat equation [6] for the considered case. The variation of amplitude value $c_{da}$ of the impurity content attained in a step versus the duration of the waiting time of a jump $t_a$, or, equivalently, versus $V_d = a/t_a$, is illustrated in figure 3. This dependence has a simple qualitative explanation. Low-mobile impurities at a short transition time $t_a$ behave as static ones, retaining the unperturbed content $c_0$. With an increase in the transition time, the amplitude content $c_{da}$ of low-mobile impurities in the dislocation core monotonically increases to the equilibrium value

$$c_{da} = \frac{c_0 \exp(\Delta E / kT)}{1 + c_0 \exp(\Delta E / kT)}.$$  \hspace{1cm} (3)

It follows from equations (1), (2) that initial deviation of $c_{da}$ off the bulk value $c_0$ at the onset of dynamic aging is described by expression

$$c_{da} \approx c_0 \exp(t_a / \tau).$$  \hspace{1cm} (4)

Clearly, this exponential increase with $t_a$ is much faster than the determined by the diffusion power-like increase. As $t_a = a/V_d$, (4) predicts strong negative rate dependence of the impurity contribution to the yield stress. As usual, the strain rate anomaly is accompanied by the temperature anomaly. Accounting for the Arrhenius temperature dependence of $\tau$ in (4), the total dependence of the impurity content in the core on $T$ may be represented as in figure 4: first $c_{da}$ increases with the increasing temperature due to the increase in the impurity mobility, furthermore, it decreases with a decrease in the equilibrium content, when the temperature increases.

For a simplified qualitative description of the temperature peak $c_{da}(T)$, one can use some interpolation formula. For example, for $c_0 < c_1$ a satisfactory approximation is given by the formula

$$c_{da}(T) \approx \frac{c_0}{c_0 + \exp(-\Delta E / kT) + \exp(-t_a / \tau)}.$$  \hspace{1cm} (5)

This dependence is shown in figure 4 by a dashed line $c_{da}$ to compare it with the result of the numerical solution of equations (1) and (2) and analytical approximations describing the low- and high-temperature branches of the peak.
4. Conclusion

An analytical theory of the dislocation dynamic aging in materials with the Peierls mechanism of the plastic deformation is developed. The theory takes into account the impurity dragging effect, which dominates over the bulk diffusion of impurities to dislocation core, thus predicting the enrichment of the impurity content at dislocations. The theory elucidates the origin of anomalies of the plastic deformation, such as negative strain rate and positive temperature dependences of the yield stress.

Figure 3. Dependence of impurity content in dislocation core on dislocation velocity $V_d$ (or on waiting time $t = \alpha/V_d$) at the parameters $c_0 = 0.1$ and $\tau_1 = \tau_0 = 10\tau$.

Figure 4. Temperature dependence of the impurity content $c_{da}$ in the dislocation core for the parameters $c_0 = 0.1$, $T_0 = 0.1E/k$, $E_1 = 1.3E$, and $t_a = 4.4 \times 10^4 \tau$. The dashed lines show: 1 the equilibrium dependence (3), and 2 the dependence characteristic of the first stage (4). The dotted line is the interpolation dependence $c_{int}$ (5).

The predicted increase in the content of low-mobile impurities as the temperature increases is responsible for various specific features in the temperature dependence of the yield stress $\sigma(T)$ in impure materials: from inflections in $\sigma(T)$ to the anomalous increase in $\sigma(T)$ in a certain temperature range. Both these features were repeatedly observed in experiments with different “Peierls” materials: in bcc metals and (in the case of prismatic slip) in hcp metals Ti, Zr, and Be and intermetallic compounds (see review in [2]). One may suppose that a sufficiently large increase of the impurity content in dislocation cores with increase of temperature (predicted by (4)) can completely block the dislocation motion and cause an interesting phenomenon known as the “inverse brittle–ductile transition,” at which a material loses its plasticity not upon cooling (as usual) but, vice versa, upon heating, as was observed in GaAs [8], or SrTiO3 [9].

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