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High-temperature recovery processes in zone-refined silver chloride

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In strain-ageing tests carried out at temperatures above about 400 K, zone-refined silver chloride shows two-stage recovery and no hardening. The activation energy of the second stage of recovery is approximately 0.25 eV and the rate-controlling process is probably the diffusion of chloride ions from jogs in screw dislocations. The duration of the first stage of recovery is shortened by raising the temperature of the test and increased by the addition of divalent impurities. It is concluded that the recovery process in the first stage is the same as that in the second stage, but is inhibited by weak impurity atmosphere formation around dislocations.

1. Introduction

Dislocations in crystals are not thermodynamically stable entities since they have self-energies that are a few eV per ion plane, while the entropy term in the expression for the free energy is very small [1]. Nevertheless, when a crystal containing dislocations is maintained at a sufficiently high temperature for a long enough period, the dislocations may arrange themselves into equilibrium arrays that do not produce long-range stresses [2]. Further, point defects present in the crystal, and which interact with the dislocations, will move to positions of minimum energy [3]. In well-annealed, melt-grown crystals, etch pit studies [4, 5] indicate that many of the grown-in dislocations line up to form an arrangement of sub-boundaries and, in the regions enclosed by these sub-boundaries – the sub-grains – there is a three-dimensional arrangement of dislocations, known as the Frank net.

When a well-annealed crystal suffers plastic deformation the equilibrium condition is disturbed and, as a result, the crystal will attempt to achieve a new condition of equilibrium. This process, in which the trend is towards the restoration of a condition of equilibrium following plastic deformation, is called strain-ageing. When this ageing occurs with the load removed it is called static strain-ageing. It is reasonable to suppose that ageing processes occur even while deformation is taking place; such a process is termed dynamic strain-ageing.

For many materials at room temperature static strain-ageing results in a hardening of the material, e.g. iron [6], NaCl:Ca [7] and NaCl:Cd [8]. However, by choosing the conditions appropriately, for example, by ageing at a sufficiently high temperature, materials often show a softening on ageing, e.g. Al [9, 10], Cu, Ni [11], Zn [12], NaCl [13].

Sometimes this softening is the result of a process, such as recrystallization, in which the crystal loses its original identity and orientation. More frequently, however, the crystal retains its identity and orientation, and softening is then the result of a local rearrangement of the defect content of the crystal. Processes of this type are described by the term "recovery".

Strong static recovery in metals is associated with narrow dislocations, i.e. with high stacking fault energy, whereas in metals with a low stacking fault energy, recovery is often difficult to observe (for a review see Cahn [14]).

For a wide range of materials, the dislocations generated during deformation (to moderate or large plastic strains) that are trapped in the test specimen form a loose cell structure: the microstructure consists, in a large part of dislocations in an interconnecting network of more or less well-developed low-angle boundaries which enclose regions with comparatively few dislocations [15].

In aluminium deformed in multiple slip, Hasegawa and Kocks [10] identified two types of recovery process: type I recovery that involves a tightening of the deformation-generated cell walls into sub-boundaries; and type II recovery which is a coarsening of the sub-grain structure. In contrast, only type I recovery was observed in both copper and nickel deformed in multiple slip [11].

A material that shows strain-age hardening around room temperature, but only recovery at liquid nitrogen temperature and also at temperatures above about 400 K, is zone-refined silver chloride (melting point $T_m = 730$ K) [16–19]. The basic test carried out by Shalitt and Sprackling is shown schematically in Fig. 1. An ageing curve (sometimes called the representative curve) is prepared by plotting $\Delta\sigma$ $(= \sigma_i - \sigma_0)$ against $\ln t_a$ for a series of tests carried out on a particular specimen. Here σ_0 is the flow stress just before complete unloading of the specimen and σ_i is the yield stress obtained on reloading after an ageing time, t_a, since the unloading.

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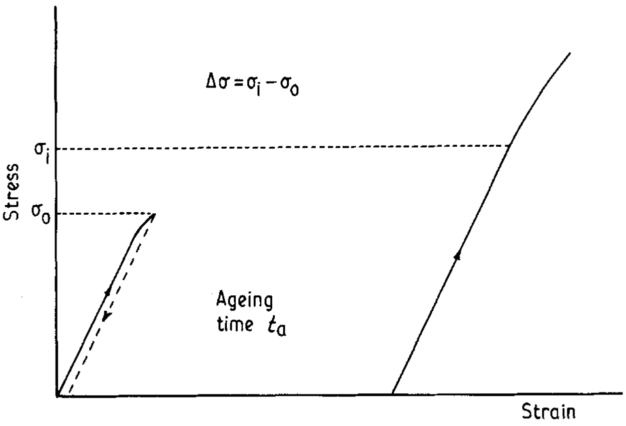

Figure 1 Schematic representation of a strain-ageing test, showing $\Delta\sigma$.

The ageing curve obtained at 500 K for zone-refined silver chloride is shown in Fig. 2. There is a continuous softening of the material with ageing time, which indicates that hardening processes are either not taking place or are swamped by the recovery processes. The curve of Fig. 2 consists essentially of two straight segments, linked by a short transition region, and for each straight segment

$$\Delta\sigma = -\alpha \ln t_a + \beta \tag{1}$$

where α and β are different constants for each segment. This paper considers the interpretation of the ageing curve for zone-refined silver chloride at temperatures greater than about 400 K. A preliminary discussion has already been given [20].

2. The formal theory of recovery

A formal theory of recovery has been produced by Cottrell and Aytekin [12], based on earlier work by Kuhlmann [21], who had suggested that recovery takes place by dislocations slipping over obstacles in their slip planes, assisted by thermal fluctuations. Cottrell and Aytekin generalized this model by assuming that, whatever the details of the recovery process, provided that it is thermally activated, the activation energy for recovery $U(\sigma)$ is a decreasing function of the stress σ and, for small ranges of σ, may be written

$$U(\sigma) = U_0 - \gamma\sigma \tag{2}$$

where U_0 and γ are constants for the range of stress chosen.

When a dislocation line segment vibrates with a frequency ν_0 the number of movements ν per unit time over a barrier of height U is given by $\nu_0 \exp(-U/kT)$, where k is Boltzmann's constant. If it is assumed that each dislocation segment movement produces an equal drop in stress, and that in a time dt the change in stress is $d\sigma$, the rate of recovery when U is given by Equation 2 is given by

$$\frac{d\sigma}{dt} = -C\exp[-(U_0 - \gamma\sigma)/kT] \tag{3}$$

where C is a constant. Integrating Equation 3 gives

$$\Delta\sigma = \sigma_i - \sigma_0 = \frac{-kT}{\gamma}\ln(1 + t_a/t_0) \tag{4}$$

where σ_0 is the value of σ when t_a is zero, σ_i that on retesting after a time t_a, and t_0 is given by

$$\sigma = \frac{-kT}{\gamma}\ln(\gamma C t_0/kT) \tag{5}$$

Equation 4 indicates that, for this class of model, provided that the change in the observed yield stress or flow stress is proportional to the change in the long-range internal stress that is locked up in the crystal, the graph of $\Delta\sigma$ against $\ln t_a$ should be a straight line when $t_a/t_0 \gg 1$, with a slope equal to $-kT/\gamma$.

The stress field within a deformed crystal is very heterogeneous. Therefore, when representing this stress field in a discussion of the thermally-activated, stress-dependent processes of dislocation motion over energy barriers, simplifying assumptions must be made. A commonly adopted approach is that suggested by Seeger [22], who wrote the resolved shear stress τ in the slip plane at the energy barrier in the form

$$\tau = \tau_G + \tau^* \tag{6}$$

In Equation 6 τ_G is regarded as a long-range internal back stress opposing τ, so that only $\tau - \tau_G = \tau^*$ is effective in assisting a dislocation held up at a short-range barrier to surmount that barrier. For silver chloride it has been shown [23] that the effective stress τ^* is practically independent of strain, though it is strongly dependent on temperature. On the basis of this result, it follows from Equation 6 that, in silver chloride, using an obvious notation,

$$\sigma_i - \sigma_0 = \sigma_{G_i} - \sigma_{G_0} + \text{constant} \tag{7}$$

so that the change in the observed flow stress on ageing under zero load is equal to the change in the long-range internal stress, apart from a constant, and

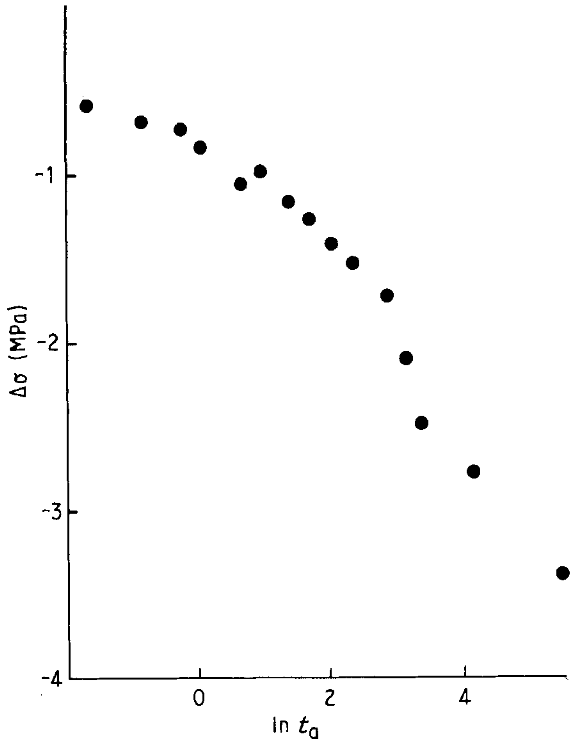

Figure 2 The ageing curve at 500 K for zone-refined silver chloride; t_a in min.

rates of change are the same. This is the justification for using the change in a flow stress, measured when the crystal is under load, to monitor processes occurring under locked-in stresses in the unloaded crystal.

Fig. 2 shows that, for deformation and ageing at 500 K, the graph of $\Delta\sigma$ against $\ln t_a$ consists of two straight segments. This agreement with the formal theory now needs to be interpreted at the microscopic level.

3. Climb-controlled recovery

Many models of recovery processes in single crystals are based on dislocation climb processes that enable dislocations to reduce the internal stresses, thereby softening the crystal, by rearranging themselves or by annihilating one another [24–26]. The driving force for the climb process is the repulsion between like dislocations in the same slip plane.

Dislocation climb in the silver halides requires the addition (or removal) of both silver and halide ions to (or from) the extra half-planes of dislocations having an edge component. The intrinsic point defects in the silver halides are cation Frenkel defects, that is, interstitial silver ions and silver ion vacancies [27]. Consequently, the concentration of halide ion vacancies will be very small and it is known that their diffusion coefficient is also very small [28]. However, it has been shown in etch pit studies on silver chloride that dislocations in bent crystals can form polygonal walls as a result of a high-temperature anneal [29, 30], a process that requires dislocation climb. Presumably, the structural disorder present in the crystal near a slip dislocation introduces a spread in the formation energies of silver ion vacancies and halide ion vacancies, so that a small concentration of halide ion vacancies is produced near dislocations. Dislocation climb may then take place.

Large-scale polygonization has not been observed in silver chloride crystals that have shown recovery at temperatures in the range 400–500 K, following axial deformation, but the activation energy for the second stage of recovery in this temperature range is approximately 0.25 eV, which is close to the value of 0.27 eV obtained by Abbink and Martin [31] for the migration energy of chloride ion vacancies in silver chloride. This is strong evidence for a recovery process governed by chloride-ion diffusion, presumably by vacancy movement.

When a dislocation is introduced into a crystal that has already undergone plastic deformation, it will experience an internal stress that is likely to have a tensile or compressive component parallel to the slip plane, the effect of which is to cause the dislocation to climb. This stress component will be called the climb stress σ_c. An edge dislocation climbs by absorbing or emitting vacancies, and jogs in the dislocation line are the most favourable sites for these processes to occur. The emission of a vacancy from a jog at a position A on an edge dislocation line (see Fig. 3), causes the jog to move one interionic distance to position B. To prevent recombination, the vacancy must then move away from this region. The activation energy for this process is U_{sd}, the activation energy for self-diffusion by vacancy migration. When the crystal is in equilibrium, vacancies leave and join the dislocation line at equal rates, the rate at which a jog emits, or absorbs, vacancies being of the order $\nu \exp(-U_{sd}/kT)$, where ν is a vibration frequency [32].

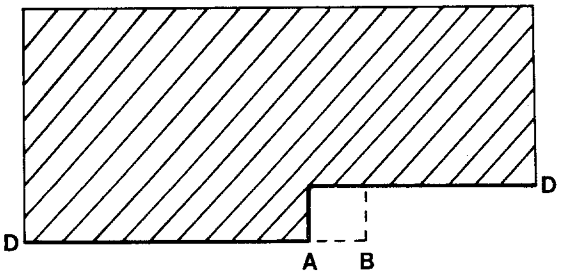

Figure 3 Vacancy emission from a jog at A on the extra half-plane DD of an edge dislocation causes the jog to move one interionic distance to position B.

For an edge dislocation to climb there must be a supersaturation, or undersaturation, of vacancies in the neighbourhood of the dislocation line. This concentration gradient of vacancies between the dislocation and the bulk crystal remote from any dislocations arises from the modification of the vacancy formation energy by the climb stress. In a region where the climb stress is σ_c, the effective energy of migration becomes $U_{sd} - \sigma_c b^3$, where b is the magnitude of the Burgers vector: $\sigma_c b^3$ is the isothermal work done by the climb stress as the jog moves from A to B. Consequently, the rate of emission of vacancies from a jog becomes $\nu \exp - [(U_{sd} + \sigma_c b^3)/kT]$ [33]. Therefore, the mean speed v_j with which a jog moves along a dislocation is given by

$$v_j = 2\,b\nu \exp(-U_{sd}/kT)\sinh(\sigma_c b^3/kT) \qquad (8)$$

If there are c_j jogs per unit length of dislocation line, the speed v_c at which the dislocation line climbs is given by

$$\begin{aligned} v_c &= c_j v_j b \\ &= c_j 2\nu b^2 \exp(-U_{sd}/kT)\sinh(\sigma_c b^3/kT) \qquad (9) \end{aligned}$$

Further, if the jogs on the dislocation line are produced thermally

$$c_j \approx (1/b)\exp(-U_j/kT) \qquad (10)$$

where $2U_j$ is the energy to form a pair of jogs. Then the expression for v_c becomes

$$v_c \approx 2\nu b \exp[-(U_{sd} + U_j)/kT]\sinh(\sigma_c b/kT) \qquad (11)$$

and it can be seen that the activation energy for the climb process is $U_{sd} + U_j$. Now, the coefficient of self-diffusion by vacancy motion D_{sd}, assuming an fcc lattice, is given by [34] $D_{sd} \approx \nu b^2 \exp(-U_{sd}/kT)$

Therefore,

$$v_c \approx \frac{2D_{sd}}{b}\exp(-U_j/kT)\sinh(\sigma_c b^3/kT) \qquad (12)$$

If $\sigma_c b^3 \ll kT$, Equation 12 may be written

$$v_c \approx \frac{2D_{sd}}{b}\exp(-U_j/kT)\frac{\sigma_c b^3}{kT} \quad (13)$$

or, since the equilibrium jog number of jogs per unit length when the dislocation is in equilibrium c_0 is given by $c_0 \approx \exp(-U_j/kT)$,

$$v_c \approx \frac{2D_{sd}\,\sigma_c b^2 c_0}{kT} \quad (14)$$

Assuming that the rate of decrease in hardness of the crystal as it recovers is proportional to v_c, and that the yield stress is linearly related to σ, the rate of change of yield stress may then be written $d\sigma/dt = -$ constant v_c which, using Equation 14, becomes

$$d\sigma/dt = -\text{ constant } \sigma \quad (15)$$

at constant temperature. Integrating Equation 15 over an ageing period t_a, during which the flow stress of the material changes from σ_0 to σ_i, gives $\ln(\sigma_i/\sigma_0) = -$ constant t_a or,

$$\sigma_i/\sigma_0 = \exp(-c't_a) \quad (16)$$

where c' is a function of temperature only. This gives an expression for $\Delta\sigma$ of the form

$$\Delta\sigma = \sigma_0[\exp(-c't_a) - 1] \quad (17)$$

which is very different from the observed ageing behaviour. Therefore, even if recovery of silver chloride involves the formation of dislocation sub-boundaries or the annihilation of dislocations of opposite sign, the results suggest that dislocation climb is not the controlling process.

4. Slip-controlled recovery

If the rate of recovery of deformed silver chloride is not controlled by dislocation climb, the alternative view is that it is controlled by the slipping of dislocations. As an example of models of this type, assume that the slip dislocations are held up by an array of parallel screw dislocations (forest dislocations) of mean spacing d as in Fig. 4. At high temperatures, the slip movement of dislocations in the crystal between forest dislocations has an almost zero activation energy. Whenever a slip dislocation cuts a forest dislocation it acquires a jog and, in the presence of an (internal) stress σ, the activation energy for the movement of the dislocation through the forest is

$$U = U_j - \sigma b^2 d \quad (18)$$

for both edge dislocations [35] and screw dislocations [36]. U_j is the energy necessary to form a jog in the moving dislocation and is slightly different for edge and screw dislocations. Substituting this expression for U in Equation 3, and assuming that the observed yield stress is linearly related to σ, gives

$$\Delta\sigma = \sigma_i - \sigma_0 = -\frac{kT}{b^2 d}\ln(1 + t_a/t_0') \quad (19)$$

where the initial stress σ_0 is related to t_0' by

$$\sigma_0 = -\frac{kT}{b^2 d}\ln\left(\frac{c'' b^2 t_0' d}{kT}\right) - \frac{U_j}{b^2 d} \quad (20)$$

and c'' is a constant.

This model predicts that a graph of $\Delta\sigma$ against $\ln t_a$ becomes a straight line at large values of t_a, with a slope equal to $-kT/b^2 d$. Fig. 2 shows that this is true for ageing at 500 K. However, the value obtained for d in the first stage of recovery is about 160 nm or about 300 interionic spacings. This value corresponds to a forest dislocation density of about $4 \times 10^{13}\,\text{m}^{-2}$, which is much higher than that of the dislocations forming the Frank net in the material which is about $10^{10}\,\text{m}^{-2}$ [5]. The difficulty is made worse if the equations are applied to the second stage of the recovery: the value for d is then about 60 nm, corresponding to a forest dislocation density of about $3 \times 10^{14}\,\text{m}^{-2}$. These values make it unlikely that, at a temperature of 500 K, either stage of recovery occurs by the movement of dislocations through an array of forest dislocations.

An alternative model may be based on the result that, for the silver halides at room temperature, edge dislocations move much faster than screw dislocations [37]. Consequently, following plastic deformation, the density of screw dislocations remaining in a crystal is much greater than the concentration of edge dislocations. If the screw dislocations introduced by deformation contain jogs, the only thermally activated process by which a screw dislocation can slip is that in which the vacancies produced by jog dragging move away from the dislocation as they are formed. The activation energy for slip, in a region of the crystal where the internal stress on the slip plane is σ, is then

$$U = U_{sd} - b^2 L\sigma \quad (21)$$

where U_{sd} is the activation energy for forming and moving away the halide ion vacancy and L is the mean jog separation. This activation energy has the same form as that in Equation 14 and, using Equation 3, will lead to jog separations of 160 nm in the first stage of recovery at 500 K and 60 nm in the second stage. The jog spacing is not equal to the forest dislocation spacing: each moving screw dislocation will have intersected many forest dislocations.

At first sight it seems unlikely that the same type of mechanism should govern both stages of recovery. The activation energy obtained for the second stage of recovery at 500 K is close to that obtained by Abbink and Martin [31] for the migration of chloride ion

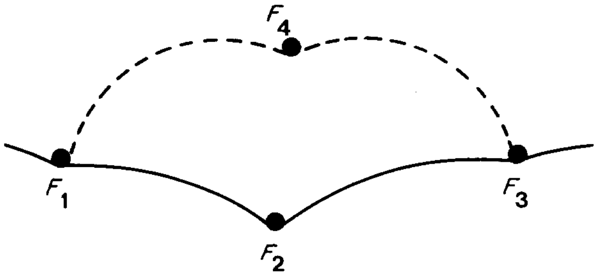

Figure 4 A slip dislocation (——) before and (. . .) after cutting through one of a forest of screw dislocations F_1, F_2, . . . of mean spacing d.

vacancies so the above mechanism is likely to be that controlling the second stage of the high-temperature recovery.

If an unjogged length of a screw dislocation moves a distance y, cutting forest dislocations with a spacing d, the number of jogs that the dislocation acquires per unit length is given by y/d^2. Assuming a jog model for the second stage of recovery, the distance that a screw dislocation needs to move in silver chloride to acquire the calculated jog density is about 1.6 mm. This distance may be interpreted as the average distance a screw dislocation moves before it becomes trapped in some way by other dislocations. It is sometimes known as the mean free path of a dislocation. Values of the mean free path of the above order of magnitude have been obtained at room temperature for LiF [38] and for LiF with 0.002% Mg [39], results which offer some support to the proposed model of high temperature recovery.

However, the mechanism suggested as controlling the rate of softening in the second stage of recovery, i.e. the diffusion of vacancies from jogs on slip dislocations, should operate from the start of ageing and should therefore occur during the first stage of recovery. This is likely to be the case. Then one mechanism of softening would operate during both stages of recovery but, for short ageing times, the effect of the recovery mechanism would be partly compensated by a hardening mechanism, and together these processes would produce two stages of recovery. The hardening process that makes the recovery appear as a two-stage process is probably the weak pinning of slip dislocations by impurities which is expected at high temperatures. The equilibrium concentration c of impurities around a dislocation in an isotropic solid is given by [40]

$$c = \left[1 + \frac{1 - c_0}{c_0}\exp(U/kT)\right]^{-1} \tag{22}$$

where c_0 is the mean impurity concentration, expressed as an atomic fraction, U is the interaction energy at the impurity site, k is Boltzmann's constant and T is the thermodynamic temperature. Equation 22 shows that c tends to the value c_0 as the temperature is raised, so that the impurities become less effective in forming atmospheres and pinning dislocations.

In support of this mechanism for the first stage of hardening, it is known that the material does contain (presumably) divalent impurity ions since, in room-temperature strain-ageing tests, considerable Cottrell–Bilby hardening is observed [10]. Further, it is observed that the duration of the first stage of recovery decreases as the temperature is raised but, at a given temperature, is increased by the addition of cadmium, as shown in Fig. 5 for ageing at 500 K.

5. Conclusion

Zone-refined silver chloride shows only one mechanism of recovery at high temperatures but, at short ageing times, a residual concentration of impurity ions inhibits this recovery and gives the appearance of a two-stage recovery process. This model indicates that highly-pure silver halide should show only one stage of recovery, and experiments are in hand to test this.

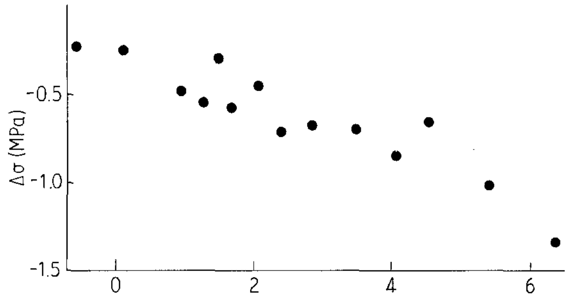

Figure 5 The ageing curve at 500 K for zone-refined silver chloride doped with 180 p.p.m. of cadmium; t_a in min.

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