

DIFFUSION AND THE MECHANICAL PROPERTIES OF SOLIDS

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I. HISTORY AND PRESENT STATUS OF THE SUBJECT

THE physics of the phenomena determining the mechanical properties of crystalline solids began to be studied relatively recently, in the 1920's. Long before that, however, an enormous amount of empirical information regarding these mechanical properties had been accumulated in different fields of technology, especially metallurgy.

The mechanical properties of even simple solids such as pure metals are strongly dependent on the previous history of particular specimens, i.e., the mechanical and heat treatment to which they had been subjected.^[1] Heat treatment affects diffusion (or self-diffusion) processes, which differ in deformed and undeformed bodies. Diffusion plays no part in deformation at low temperatures; however, the state of a body and its mechanical properties are changed by subsequent heating to a temperature at which diffusion begins to occur.

Both diffusion and the mechanical properties of solids are structure-sensitive, being intimately related to structural details including the microstructure, and especially to defects of the atomic structure (departures from the regular arrangement of atoms in crystal lattices).^[2] It became possible to determine the atomic structure experimentally only after x-ray diffraction by crystals was discovered by Laue, Friedrich, and Knipping in 1912. Prior to that the metallographic microscope had been used for over 100 years to determine the microstructure of metals and alloys, thus making it possible to draw conclusions regarding their mechanical properties and even to predict such properties and their changes after heat treatment of alloys, for example.^[3] This description of the microstructure, which is still important, is to a considerable degree only qualitative and is limited in certain respects. Specifically, changes occurring in metals after plastic deformation and strongly affecting their mechanical properties (cold-working), are not observed directly under a microscope. On the other hand, it must be mentioned that very recently, following the development of special etching techniques for revealing dislocations,^[4] the microscopic study of deformed bodies has acquired new importance and has become a source of important information regarding the structural changes that follow deformation. However, the development of physical ideas regarding mechanical properties required an account of the

atomic structure of crystals and the development of the crystal-lattice theory (M. Born, 1915), as a basis for comparing observed properties with the calculated cohesive forces.

The very first investigations of residual deformations in single crystals, at the beginning of the 1920's, revealed a sharp disagreement between the theory and the practical behavior of crystals. In 1922 Mark, Polanyi, and Schmid^[6] published their famous paper on the stretching of zinc single crystals. They found that deformation results from slip, involving the relative tangential displacements of parts of a crystal in the basal (0001) plane and in the [1120] crystallographic direction. A permanent deformation results when a critical shearing stress in the slip plane is exceeded; this depends both on the applied force and on the orientation of the given plane. Even earlier, in 1918, fundamental studies were begun by A. F. Ioffe and his co-workers,^[7,8] who for the first time used x rays to investigate structural changes in plastically deformed crystals. In this work it was clearly shown that deformation results in imperfections of crystal structure, which are revealed by the so-called "asterism" of Laue patterns. Ioffe's experiments were intended to test Born's theory. Since the theory had been worked out quantitatively only for ionic crystals, Ioffe's experiments were performed on rock salt crystals, which are of no practical importance but are of extreme interest for a comparison with the theory. It was learned that the basic effects observed in sodium chloride are the same as in metal crystals. In the experiments on sodium chloride it was possible to use various supplementary techniques (optical, electrical, and photoelectric); this was of considerable assistance in accounting for the observed complicated effects. Ioffe's experiments showed that deformation through slip along definite crystallographic planes and in definite directions (the (110) plane and [110] direction in sodium chloride) is accompanied by the appearance of subgrains (mosaic blocks) turned relative to the bulk of the crystal through angles increasing with the extent of deformation. Plastic deformation begins only when a critical shear stress in the slip plane is exceeded; this is the flow stress or yield point, which is dependent on temperature. It was found subsequently that the yield point depends on the sensitivity of the technique used to measure deformation. The "x-ray yield point" of NaCl at room temperature is a few hundred grams per mm². When the first traces of slip are detected optically (from birefringence observed with crossed

Nicol prisms) the value obtained is only a few tens of grams per mm^2 . Even lower values are obtained by observing changes in photoconductivity. According to Ioffe's results the yield point is lowered with increasing temperature, and vanishes at the melting point, whereas the fracture strength (the critical normal stress resulting in fracture) is constant over a broad temperature range. Therefore at low temperatures, where the tensile strength is below the yield point, a crystal is brittle (breaks without appreciable plastic deformation), while at high temperatures it becomes plastic (fracture is preceded by plastic deformation, which increases with temperature). These results provide the basis for the "Ioffe scheme" according to which brittleness or plasticity is not an inherent property; a body is plastic or brittle depending on the relationship between its tensile strength and yield point, and transitions from one state to the other can occur as the temperature changes. Of course, in the case of an extremely low yield point detected by very sensitive methods of measuring deformations, brittleness is not to be understood in the absolute sense but as corresponding to very small plastic deformation. The Ioffe scheme is only approximate, since it does not take account of forms of low-temperature deformation (twinning) besides slip, and neglects hardening effects, the rate of deformation etc. Cold-shortness was found to be too complex to be accounted for by the scheme. However, the Ioffe scheme has retained its qualitative significance until the present time.^[80]

Of especially great interest were Ioffe's famous experiments,^[8] in which the strength of fracturing sodium chloride crystals was determined as the crystals dissolved in water. These experiments confirmed for the first time the theoretical strength calculated from cohesive forces. Born's theory predicted tensile strengths two to three orders of magnitude greater than the experimental results. In the case of sodium chloride the theoretical value was 200 kg/mm^2 , while $\sim 0.5 \text{ kg/mm}^2$ is observed for the usual fracture of rock salt in air. In Ioffe's experiments on dissolving rock salt the observed tensile strength was as high as 160 kg/mm^2 , thus approaching the theoretical value. Ioffe interpreted his results as follows. A dry crystal breaks prematurely because of the presence of incipient cracks with high stress concentrations at their edges. With the dissolution of the surface layer, in which most cracks are located or originate, a crystal is able to withstand a tensile pull close to the theoretical magnitude. This explanation follows Griffith's theory,^[9] which had been advanced previously to account for the low technical strength of glass, and which was based on the strength of glass containing artificially induced cracks. The observed (technical) tensile strength σ and crack length λ are related by Griffith's formula

$$\sigma\sqrt{\lambda} = \text{const} \cong \sqrt{E\alpha}, \quad (1)$$

where E is the elastic modulus and α is the surface tension.

It must be mentioned that the foregoing interpretation of Ioffe's experimental results was disputed in the literature and can still not be regarded as firmly established. For example, it was contended that the observed high strength results from a secondary effect—hardening following the considerable plastic deformation that occurs in a salt while dissolving in water. However, as Born correctly observed at the time,^[10] it is significant, independently of the attendant effects, that when a crystal fractures in a non-precision mechanical device cohesive forces determined from atomic constants come into play. The correctness and farsightedness of this conclusion have been confirmed brilliantly in recent years. Under different conditions (in single-crystal whiskers) a number of metals have exhibited very high tensile strength approaching the theoretical values. For example, the strength of iron whiskers 2μ in diameter is as high as 1350 kg/mm^2 .^[11,12]

Thus, one of the two clear principal contradictions between Ioffe's experimental results and the crystal-lattice theory, the discrepancy regarding tensile strength, was considerably modified by the fact that the theoretical strength can be approached under special conditions. The second disagreement was the observed occurrence of permanent deformation through slip. Born's theory of ideal crystals has no place for the experimentally observed deformation. Frenkel^[13] made a detailed analysis of the possibility of slip in ideal crystals within the framework of Born's theory, and showed that slip along an atomic plane requires that two parts of a crystal be separated by a distance of the order of the atomic spacing. Frenkel employed a "two-saw" model with the teeth of one saw inserted between the teeth of the other saw. Relative motion of the "saws" requires that they be separated by a distance equal to the height of the teeth. A calculation showed, however, that this slip mechanism in an ideal crystal requires extremely high stresses only one order of magnitude smaller than the elastic modulus. Therefore the slip observed in real single crystals under extremely low stresses cannot be accounted for by the theory of ideal crystals.

Ioffe's investigations of the mechanical properties of sodium chloride were continued in the experiments of Obreimov and his co-workers,^[14] who used an optical method and observed birefringence, caused by internal strains, near slip planes. It was shown by this optical method that slip traces appear in sodium chloride at a stress of $\sim 30 \text{ g/mm}^2$. It was important that the first slip traces observed through crossed nicols do not appear immediately in their entire length but propagate with a definite velocity from one face to another.

During the 1920's and 1930's in both the U.S.S.R. and abroad,^[86] an enormous amount of diversified work was done on the mechanical properties of different single crystals, both nonmetallic (NaCl, AgCl, etc.) and metallic (mainly low-melting Zn, Cd, Mg, Al, Pb, Sn, Bi, and their alloys Cd-Zn, Sn-Zn, Al-Mg, Zn-Mg, as well as α iron, W, Cu-Ni, Cu-Zn, etc.). These studies cleared up the geometry of slip effects as related to crystallographic orientation, the relationship between hardening by plastic deformation and the deformation rate and temperature, and also the attendant recovery and recrystallization effects. Detailed summaries of the work done abroad can be found in ^[15,16]. An account of extremely interesting discontinuous deformation is given in ^[17]; an explanation of these effects is given in ^[18]. Stepanov^[19] made important observations of the dependence of the strength of sodium chloride single crystals on the shape of specimens and on crystallographic orientation. Many other important results cannot be discussed here. However, the source of the principal disagreement between the theory of crystal lattices and the practical behavior of crystals was cleared up very slowly.

Taylor^[20] in 1934 was the first to advance the quantitative hypothesis of edge dislocations, which cause slip by moving through a crystal. The origin of dislocations and the conditions governing their motion were not considered in this early work. The quantitative description was intended to account for the hardening that accompanies plastic deformation, which was described as the result of interactions between dislocations. It was shown that the stress required for the motion of a single dislocation must increase with the density of dislocations as a deformation is augmented, since elastic forces acting between dislocations hinder their motion. During the same period other investigators^[20] also suggested that plastic deformations in crystals result from the motion of dislocations.

The dislocation theory, which was at first purely hypothetical, was developed by many authors including the Burgers brothers,^[21] Frank,^[22] Read,^[23] Shockley^[24] and others. An important contribution was made in 1938 by Frenkel, who in collaboration with T. A. Kontorova^[25] for the first time used a two-dimensional atomic model to discuss the motion of dislocations. Eshelby^[26] subsequently confirmed their results for the three-dimensional case. The formulas derived in ^[25] show that the velocity limit of dislocation motion is the velocity of sound, which here plays a part analogous to that of the velocity of light in relativity theory.

At the present time dislocation theory has been so extensively developed that a systematic account has been given in special monographs^[27,28] and a detailed account is given in every serious work on metal theory.^[29,30]

The dislocation theory was not developed only in connection with plastic deformation. It was also used to interpret crystal growth^[31] and the effects connected with annealing and the recrystallization of deformed bodies. The triumphant confirmation of this theory came with the experimental observation of dislocations and their movements, at first optically using special etching techniques,^[32] and later by electron-microscope^[33] and x-ray^[34] methods. Dislocation theory, which is based on the existence of line defects (edge and screw dislocations), successfully accounts for plastic deformations in crystals and the attendant hardening effect. The laws of the dislocation growth of crystals have been confirmed experimentally. The theory accounts convincingly for polygonization and the formation of small-angle dislocational boundaries in deformed crystals after heating. The theory considers different effects resulting from dislocation interactions, such as splitting into partial dislocations with the formation of stacking faults, the piling-up of dislocations in a single slip plane at obstacles such as grain boundaries, the intersection of dislocations in different planes to form immobile Lomer dislocations, the intersection of moving screw dislocations with the resultant formation of jogs on dislocations and the appearance (following motion) of lattice vacancies and interstitial atoms etc.

The basic importance of dislocation theory lies in the fact that it has reconciled the disagreement between the theory of ideal lattices and the experimentally observed deformations resulting from slip or twinning, and that it describes the departures from ideal lattices that accompany the observed deformation effects. It must be acknowledged, however, that despite the development of various schemes and models of dislocation arrangements, the theory is still only a theory of dislocations and not a theory of mechanical properties.^[87] We are still left with important unanswered or controversial questions such as the generation and multiplication of dislocations,^[35] the insufficiently understood conditions for the creation of various aggregates of different dislocations etc. The consistent description of mechanical properties on the basis of dislocation theory is still in an early stage; its completion lies in the future. At the present time, however, it would be difficult to overestimate the fruitfulness and importance of dislocation concepts for interpreting the observed mechanical properties of solids.

It is especially important to note the more recently developed theory that dislocation mechanisms are involved in fracture as well as in deformation. A number of models have been proposed^[36] to show how relatively stable (not collapsing spontaneously) incipient cracks, whose growth leads to fracture, can originate and develop in crystals through the formation of dislocation pile-ups and through intersections or other interactions between dislocations. Disloca-

tion theory is thus becoming a very broad basis for the interpretation and description of mechanical properties.

The entire foregoing discussion pertains to non-thermal mechanical properties of crystals. However, as already mentioned, the mechanical properties of solids, especially at high temperatures, are intimately related to diffusion phenomena. Diffusion effects are especially important in creep at high temperatures and in the so-called sintering effect of metallic and nonmetallic powders, which are compacted by capillary forces resulting from permanent deformations induced by diffusion.

The influence of diffusion on the generation, motion, and stability of dislocations still remains largely unclarified. Knowledge of the diffusion or self-diffusion mechanism is of fundamental importance in this connection. A correct understanding was first attained by Frenkel,^[37] who showed that thermal motion in crystal lattices produces vacancies and interstitial atoms, and that diffusion (especially self-diffusion), at least in metals, alloys, and crystals of inorganic compounds, is a random process whereby lattice vacancies are replaced successively by atoms or ions. It must be emphasized that some other authors have proposed different diffusion mechanisms such as "ring exchange" of atoms.^[81] However, the more recently observed diffusion porosity (the precipitation of excess vacancies as pores) accompanying unequal partial heterodiffusion,^[38] which is rightly called the Frenkel effect, leaves no doubt that the Frenkel vacancy mechanism of diffusion is correct.

Vacancies existing in a lattice must interact with dislocations. Each dislocation is surrounded by a field of elastic stresses. For this reason the equilibrium concentration of vacancies around dislocations is not identical at different points. At temperatures high enough for diffusion, currents of vacancies or atoms must arise, leading to the "healing" (annihilation) of dislocations. Dislocations generated and multiplying in a crystal through the action of external forces are nonequilibrium structures; at high temperatures they must either grow or disappear, thus restoring the regular periodic arrangement of atoms.

The only diffusion effect that has thus far been treated quantitatively in dislocation theory is the climb of dislocations, which comes about through the joining of linear arrays of atoms or vacancies parallel to a dislocation axis. Mott^[39] used this effect to account for the so-called vertical dislocational walls forming small-angle subgrain boundaries. Weertman^[40, 41] recently attempted a calculation, based on this effect, of high-temperature creep in metals (see below). It must be mentioned that interactions between vacancies and dislocations in a system containing intersecting screw dislocations is complicated by the possibility that excess vacancies will be produced through the motion of intersecting dislocations.

Interactions between vacancies and dislocations are important for diffusion as well as for effects associated with mechanical properties. It has been found experimentally that in both metallic and nonmetallic crystals subjected to plastic deformation or having lattice irregularities due to crystallization, diffusion processes are accelerated, often hundreds or thousands of times.^[85] The simplest explanation of this result on the basis of the Frenkel diffusion theory is that in these systems, at the temperatures of fairly rapid diffusion, the restoration of lattice regularity produces a large number of excess vacancies promoting accelerated diffusion. The change in the micro-pattern of diffusion, resulting from the presence of dislocations, undoubtedly plays a definite part in these effects. The influence of dislocations on diffusion is still not actually understood.

The velocity of thermally fluctuating movements of atoms in crystals increases exponentially with temperature. At very high temperatures we can expect a reduced stability of dislocations, which can be destroyed by climb and the mutual annihilation of dislocations with opposite signs, and by thermal-diffusion "resorption." At the highest (near-melting) temperatures in crystals we can therefore expect diffusion to play an increasingly important part in plastic deformation. Frenkel in 1946^[42, 43] pointed out the possibility of permanent deformations at such temperatures purely as a result of atomic diffusion. This hypothesis was applied to sintering, which Frenkel interpreted as a result of viscous flow under capillary forces through a self-diffusion process similar to that in liquids (by successive random motions of individual atoms). The treatment of sintering as a result of diffusional creep in crystals was subsequently confirmed by a pure diffusion calculation of directed self-diffusion in a system of contiguous pressed-powder particles, i.e., in a porous body, where capillary forces around pores produce a negative pressure that induces currents of directed atomic self-diffusion fully equivalent to viscous flow.^[44] Evidence has recently appeared that such viscous flow occurs at near-melting temperatures in metals under external forces through a pure diffusion mechanism, since no signs of dislocational deformation appear.^[71]

The foregoing necessarily brief review shows that despite great advances in the understanding of effects that determine mechanical properties and diffusion in solids, we still lack an understanding of many important relations without which a quantitative description of the occurring regularities is impossible. It is appropriate to note that the Frenkel hypothesis played an essential part in the development of fundamental concepts, especially with regard to diffusion and diffusional (non-dislocational) deformation, as well as with regard to the kinetics of dislocation motion in plastic deformation through slip and twinning. We shall consider more thoroughly certain manifestations

of deformation in crystals that occur at high temperatures and are associated with diffusion processes involved directly in deformation. The kinetics of deformation and the diffusion effects are intimately related.

II. STEADY-STATE CREEP OF METALS AT HIGH TEMPERATURES AND DISLOCATION CLIMB

The phenomenological laws of deformation through creep, observed at a constant applied stress, are similar for different kinds of solids. Qualitatively similar regularities are observed in metals and nonmetals, single crystals and polycrystals, and in noncrystalline bodies such as plastics.^[43] The time dependence of deformation, at a constant applied stress, includes three principal stages: 1) unsteady or diminishing creep, 2) steady-state creep with a constant deformation rate, and 3) accelerated creep ending in fracture. In different kinds of solids the physical processes during each stage are different but result in similar regularities. We shall hereafter confine our attention to creep in metals. The durations of the different creep stages and the magnitude of the deformation induced in each stage within any given material depend on temperature and the applied stress. As the temperature or stress is reduced the steady-state rate of creep diminishes, the duration of the steady-state creep stage is lengthened, and the third stage of accelerated creep may not be reached at all. On the other hand, with increasing temperature and stress, the steady creep rate increases sharply and the deformation is augmented in each stage; the third stage, ending in fracture, is reached relatively rapidly. It must be emphasized that creep, especially in metals, does not occur only at high temperatures, but produces an appreciable effect even at moderate temperatures far below the melting point. Even at such temperatures creep undoubtedly involves both slip resulting from dislocation movements and diffusion effects whose presence has frequently been confirmed indirectly (as by the accompanying polygonization, which is known to result^[28] from the diffusional climb of dislocations). The mechanism of the steady-creep stage is of fundamental importance. With regard to the first and third stages, although the details of the atomic mechanism still require experimental clarification, a general qualitative interpretation of the processes already exists. In the third stage accelerated deformation is associated with the development of local imperfections or, sometimes, partially with recrystallization processes that reduce hardening.* The first, unsteady, stage depends on effects similar to cold working. The first stage is often described by means of the so-called "exhaustion theory," according to

*The motion of grain boundaries in polycrystalline specimens resulting from a recrystallization deformation, does not lead directly to elongation but enhances the plasticity of the material (see^[79]).

which there are volume elements with unequal "activation stresses" (the difference between the flow stress and the applied stress); these elements require thermal fluctuations of different magnitudes to produce local creep.^[28]

Weertman^[40,41] recently proposed a theory of the steady-state creep stage at medium temperatures using an atomic model of dislocation climb to describe the process. He has evidently accounted correctly for the macroscopic laws of creep in metals (the dependence of the steady creep rate on temperature and the applied stress).

Weertman's theory considers a dislocation array immobilized by an obstacle after being emitted from a source (such as a Frank-Read source) acted on by an applied stress. In the case of metals having several intersecting slip systems the obstacles can be immobile (Lomer) dislocations produced through the interactions of dislocations belonging to different systems. According to this theory, when an obstacle stops a group of n dislocations the elastic stress acting on the leading dislocation is multiplied by the factor $n = 2\sigma L/\mu b$, where σ is the applied stress, L is the width of the immobilized group (the distance between the Frank-Read source and the obstacle), b is the Burgers vector, and μ is the shear modulus (^[28], p. 128). It follows from energy considerations that the leading dislocation can climb through a distance $h = 2\tau/nb\sigma = \tau\mu/\sigma^2 L$, where $\tau = \mu b^2/12\pi(1-\nu)$ and ν is the Poisson coefficient.

Climb is described as the result of vacancy diffusion to the dislocation axis because of the vacancy concentration gradient, which in turn is caused by the elastic stress gradient created by the dislocations. The equilibrium concentration of vacancies around the stopped leading dislocation (belonging to the group of n dislocations) will be $N_e = N_0 \exp(\pm n\sigma b^3/kT) = N_0 \exp(\pm 2L\sigma^2 b^2 \mu kT)$, where N_0 is the equilibrium concentration in the absence of dislocations, since the work of forming vacancies near the leading dislocation is increased or decreased by the amount $n\sigma b^3$ (depending on the sign of the dislocation). Assuming that immobilized dislocations are of both signs with equal frequency, dislocation climb can be described as vacancy diffusion between the two closest leading dislocations of two immobilized groups with opposite signs; the vacancy concentration between the two given dislocations is assumed to be N_0 . For steady diffusion $[(d/dr)(r dN/dr) = 0$, where r is the distance along the normal from the leading dislocation] the vacancy concentration is represented approximately by

$$N = N_0 + \frac{(N_e - N_0) \log\left(\frac{r_1}{r}\right)}{\log\left(\frac{r_1}{r_0}\right)},$$

where r_1 is half of the mean distance between immobilized dislocation arrays and r_0 is the distance to

which the stress field maintains the stress concentration N_e . The vacancy flux per unit length along the dislocation axis is $2\pi rD'(dN/dr)$, where D' is the vacancy diffusion coefficient; this flux approximately equals $N_0D'nob^3/kT$ when $nob^3/kT < 1$. This flux produces the climb rate $I = N_0D'\sigma b^5/kT = 2N_0D'\sigma Lb^4/\mu kT$. When the rate and height of climb are known, the creep rate can be computed. Let M be the number of active Frank-Read dislocation sources per unit volume, λ the distance that the edge component of a dislocation loop advances from a barrier, λ' the corresponding distance for a screw dislocation. We can then write $V = IM\lambda\lambda'(b/h)$ for the creep velocity, i.e.,

$$V = \frac{n^2\sigma^2b^7N_0D'\lambda\lambda'M}{2\pi kT} \cong \frac{30\sigma^4b^3N_0D'\lambda\lambda'ML^2}{\mu^2kT}, \quad (2)$$

where $nob^3/kT < 1$. Similarly, when $nob^3/kT > 1$ we obtain

$$V \cong 15\sigma^2bN_0D'\lambda\lambda'M\mu^{-2}L \exp\left(\frac{2\sigma^2Lb^2}{\mu kT}\right). \quad (2a)$$

In order to determine the dependence of V on σ it is necessary to determine how the factors M , L , λ , and λ' depend on σ . Weertman's reasoning in this connection depended partially on experimentally known relations. He assumed that M is independent of the applied stress, since according to data in [76] M is practically constant for stresses exceeding the critical shear stress in the absence of dislocation interactions inducing hardening. For a regular single crystal of small cross section Weertman assumed that the product of λ and λ' equals the crystal cross section and is independent of the stress. In polycrystalline specimens λ probably equals the average diameter of subgrains, while λ' is the grain diameter, since it is difficult to conceive of obstacles to the propagation of pure screw dislocations within grains. In this case the dependence of λ on σ is obtained from experimental results in [46], according to which subgrain diameters in aluminum are proportional to $\sigma^{-2/3}$ independently of temperature.

The dependence of L on σ was computed from the following considerations. The shear stress resulting from immobilized dislocation loops decreases approximately as $4\sigma L^3/R^3$, where R is the distance from the center of a loop. If the activation stress of a Frank-Read source is $\bar{\sigma}$, the available stress can activate a source in another slip system, the source being located in a cylinder of height $2L$ and radius $4L(\sigma/\bar{\sigma})^{1/3}$. A Lomer dislocation can then appear closer to the first source; this would represent a reduction of L . The condition on L is that the product of the source density M multiplied by the volume within which the shear stress is greater than σ must be smaller than unity. This leads to the equation

$$L \cong \frac{1}{2} \left(\frac{\bar{\sigma}}{\sigma} \right)^{2/3} M^{-1/3}.$$

Thus the product $\sigma^4\lambda\lambda'ML^2$ in the formula for V

must, according to Weertman, contain the factor σ to about the fourth power in a single crystal and to about the third power in polycrystals.

The temperature dependence of V is given practically by the product N_0D' , which represents the self-diffusion coefficient and is represented by the formula $N_0D' = D = \nu_0/b \exp(S/k) \exp(-Q/kT)$, where Q is the activation energy for self-diffusion, S is the entropy of self-diffusion activation, and ν_0 is the maximum frequency of atomic vibrations in the lattice. Thus the activation energy for steady-state creep must equal the activation energy for self-diffusion.

The foregoing theory, in which the obstacles to dislocation motion are regarded as immobile Lomer dislocations, pertains only to crystals possessing several slip systems. It does not apply, for example, to hexagonal crystals where slip is observed only in the basal plane. (Weertman points out that even in hexagonal crystals exhibiting prismatic and pyramidal slip the Burgers vector of the corresponding dislocations also lies in the basal plane; therefore immobile Lomer dislocations are not formed.) In a later article [41] Weertman proposed a somewhat different and more general mechanism of creep, also applicable to crystals with a single slip system. Here we consider parallel arrays of dislocations from sources located in different planes (Fig. 1). The leading dislocations of each array can be held up by dislocations of opposite sign in the following array; this prevents their progress if the arrays are close. In this model the rate of climb of dislocations I_1 is given by

$$I_1 = \left(\frac{\nu_0 N_0 \sigma b^4}{kT} \right) \exp\left(\frac{S}{k}\right) \exp\left(-\frac{Q}{kT}\right), \quad (3)$$

where S and Q are the entropy and activation energy, respectively, of self-diffusion, assuming that an equilibrium concentration can be established near the dislocations. If thermal equilibrium cannot be established for vacancies directly, it can be achieved by the presence of jogs on dislocations (in which case, as we know, vacancies are produced or annihilated as dislocations move). [28] When vacancies appear or disappear only in the presence of jogs, the creep rate is given by

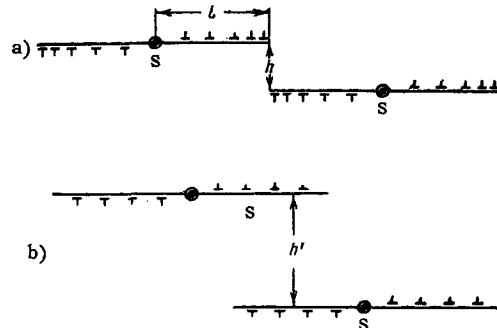


FIG. 1. Blocked (a) and moving (b) dislocation loops from two sources in parallel planes. [41]

$$I_2 = \left(\frac{L}{b}\right) \left(\frac{v_0 N_0 \sigma b^4}{kT}\right) \exp\left(\frac{S^*}{k}\right) \exp\left(-\frac{Q^*}{kT}\right), \quad (3a)$$

where S^* and Q^* are the sums of the entropies and activation energies, respectively, for self-diffusion processes and jog formation. Here $2L$ is the distance between dislocation sources lying in parallel planes (Fig. 1); $n = 2\sigma L/\mu b$ is the number of immobile dislocations in the group. The formula for I_2 is based on the assumption that the jog concentration corresponds to thermal equilibrium. Jogs can be formed both by thermal excitation and by the intersection of dislocations in different (relatively inclined) planes. Jogs formed in the second manner will not be annihilated by climb if a component of their vector sum is perpendicular to the slip plane. When only a small amount of energy is required for the formation of a jog, I_1 is practically correct for the rate of climb.

The given model yields another relation for the height h of dislocation climb (Fig. 1). Here leading dislocations are annihilated through climb and are replaced by new dislocations from the source; creep is maintained in this manner. Two groups of dislocation loops in different slip planes can also move with respect to each other without climb or annihilation if the plane separation h exceeds $\mu b/4\pi\sigma$. The magnitude of h is approximated in this way. Weertman uses the following considerations to determine L . A cylinder of height $2h$ and radius $2L$ containing a group of dislocation loops propagating from a single Frank-Read source should on the average contain three more Frank-Read sources immobilizing this group of loops. We should thus have $8\pi ML^2 h/3 = 1$, where M is, as previously, the density of dislocation sources. We thus obtain

$$L^2 = \frac{3}{8\pi M h} = \frac{3\sigma}{2\mu M b}.$$

The creep rate, as above, is the product of the dislocation source density, the mean area swept out by a dislocation loop ($4\pi L^2$) multiplied by b , the climb velocity of leading dislocations, and the reciprocal of the height of climb ($1/2h$). The creep rate under small stresses is

$$V = \left[\frac{3(6)^{1/2} \pi^2 v_0 b^{3/2} \sigma^{9/2}}{M^{1/2} \mu^{7/2} kT} \right] \exp\left(\frac{S}{k}\right) \exp\left(-\frac{Q}{kT}\right) \quad (4)$$

or, more generally,

$$V = \left(\frac{6\pi^2 v_0 \sigma^2}{\mu^2}\right) \text{sh} \left(\frac{3^{1/2} \sigma^{5/2} b^{3/2}}{2^{1/2} \mu^{3/2} M^{1/2} kT}\right) \exp\left(\frac{S}{k}\right) \exp\left(-\frac{Q}{kT}\right). \quad (4a)^*$$

When the energy of jog formation is large, S and Q are the respective sums of the entropies and activation energies for self-diffusion and jog formation.

We see from the foregoing discussion that both versions of Weertman's theory furnish essentially only an estimate of the rate of steady-state creep, since despite the clear and definite model of the atomic mech-

*sh = sinh.

anism, the calculation requires additional simplifying assumptions and a number of quantities in the formulas are determined very approximately. There can therefore be no claim of quantitative agreement between this theory and experiment. Nevertheless, considerable interest attaches to the derived power relation between the rate of steady-state creep and the applied stress (with the powers 3 and 4.5 in the two versions of the theory), and to the exponential dependence on the reciprocal of absolute temperature. Both theoretical predictions are confirmed experimentally in general over a broad temperature range when the applied stress is not too small.

Figure 2 shows the experimental dependence^[47] of the rate V of steady-state creep on the stress σ at several temperatures for polycrystalline (cermet) specimens of copper, nickel, and iron. The coordinates are $\log_{10} V$ and $\log_{10} \sigma$. At relatively high values of σ we observe the power law $V \sim \sigma^n$, where the exponent n is practically identical for the three metals at all temperatures ($n = 4.6-4.8$). At small values of σ the slope of the straight line is decreased,

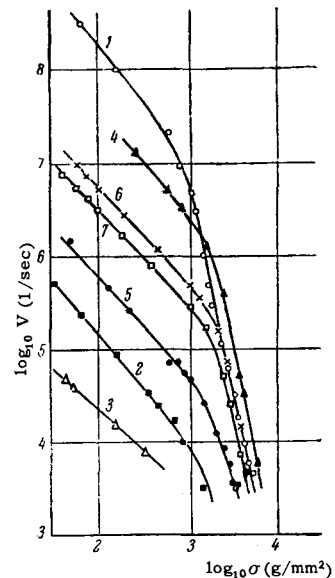


FIG. 2. $\log_{10} V = f(\log_{10} \sigma)$ for specimens of Cu, Ni, and Fe.^[47] Straight-line segments are seen for small σ ($V \sim \sigma^n$) and large σ ($V \sim \sigma^m$). 1 - Cu: 600°, $n = 1.3$, $m = 4.8$; 2 - Cu: 900°, $n = 1.2$, $m = 4.8$; 3 - Cu: 1040°, $n = 1$; 4 - Ni: 900°, $n = 1.2$, $m = 4.6$; 5 - Ni: 1100°, $n = 1.1$, $m = 4.6$; 6 - Fe: 1100°, $n = 1.1$, $m = 4.8$; 7 - Fe: 900°, $n = 1.1$, $m = 4.8$.

with an approach to linear dependence. It will be seen (Sec. IV) that this represents a gradual change of the creep mechanism—a reduced role for climb and the appearance of a pure diffusion mechanism, with deformation induced by successive random movements of individual atoms.

The power-law relation between the creep rate and the stress was also confirmed experimentally^[40] for Al, Sn, and Pb, with n varying from 3 to 5.5. For the

alloy Ni + 40% Cu deformed at 700°C under stresses from 2 to 9 kg/mm², $n = 3.6$.^[48]

It must be mentioned here that the experimental data for dependence of the steady-state creep rate on stress, which data are represented satisfactorily by a power law, are also fitted in most cases by an empirical formula in which V depends exponentially on σ . When $\ln V$ is plotted as a function of σ (Fig. 3), over a large range of σ we obtain a straight line represented by

$$V = V_0 \exp \left(-\frac{U_0 - \gamma\sigma}{kT} \right), \quad (5)$$

where U_0 , γ , and V_0 are constants ($U_0 = Q$ is the activation energy for creep), k is Boltzmann's constant, and T is the absolute temperature. This form of the relationship between V and σ is often used when the creep rate is studied in conjunction with τ , the load-endurance interval in long-time strength (Sec. III).

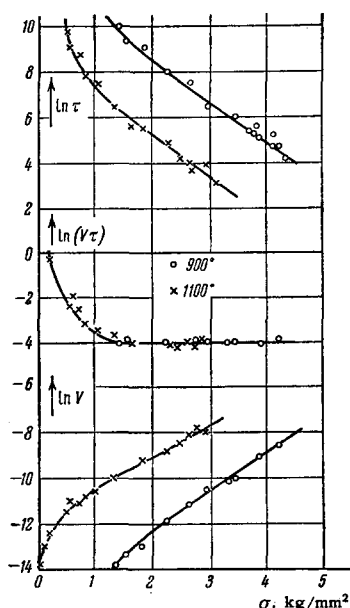


FIG. 3. Plots of $\ln V$, $\ln \tau$, and $\ln(V\tau)$ vs. σ for Ni.^[47]

These quantities vary experimentally so that $V\tau = V_0\tau_0 = \text{const}$ and τ obeys the exponential law (6) (Sec. III). It is still not clear whether the constancy of the product $V\tau$ indicates the concurrence of the processes governing creep and long-time strength or only that parallel laws govern the two processes.

It should also be noted that (5) for the creep rate V and (6) for τ are not always confirmed experimentally. For small σ , especially at high experimental temperatures, deviations of each quantity separately and an inconstancy of the product $V\tau$ are observed (Fig. 3). These results may possibly indicate a transition to a different deformation mechanism, such as pure diffusion without participation by dislocations (Sec. IV); this is still an open question.

The exponential dependence of the rate of steady-

state creep on the reciprocal of the absolute temperature has also been confirmed frequently. In many instances^[49] the activation energy for creep coincides with the activation energy of self-diffusion known from direct measurements of self-diffusion kinetics. Certain investigations of specimens preserving distortions and lattice imperfections have yielded values smaller than those for the activation energy of self-diffusion.^[50] It was found recently in^[51], where a study was made of the creep of α iron in torsion at 630–900°C in the stress range 40–439 kg/cm² that under stresses 40–138 kg/cm² the activation energy for creep is independent of stress and amounts to 77.7 kcal/g-atom, which considerably exceeds the activation energy for self-diffusion (~ 58 kcal/g-atom). The authors assume that in the given interval the activation energy is the sum of the self-diffusion activation energy and the energy of jog formation. At higher stresses the activation energy was reduced drastically to 50 kcal/g-atom; this effect was not accounted for. Similar results have not been obtained in other investigations.

It should be mentioned that the absolute values of the activation energy Q given in different publications must be used with care. To obtain a true value of Q the temperature dependence of the pre-exponential factor must be known; otherwise, the value obtained for Q can be appreciably erroneous.^[52]

This consideration plays no part only when the activation energy is obtained from experiments in which the change of the steady-state creep rate is determined for a rapid (or sudden) relatively small temperature change (by 20–30°^[89]).

Creep in extremely pure (99.99%) monocrystalline and polycrystalline copper in the temperature range 400–700°C has been studied thoroughly in^[88]. It was found that the activation energy for steady-state creep (determined as in^[89]) in single crystals is 49 kcal/g-atom, and thus does not differ from the activation energy for self-diffusion. Different results were obtained for polycrystals. Representing the creep rate V as a function of absolute temperature T and stress σ by the formula $V = V_0(T) \exp [-(Q - \gamma\sigma)/kT]$ [see Eq. (5)], two sets of the constants V_0 , Q , and γ were obtained at each temperature; these were associated with stresses lying below or above a certain critical stress $\sigma'(T)$. At 400–500°C the activation energy Q for $\sigma > \sigma'$ and $\sigma < \sigma'$ was 32 and 28 kcal/g-atom, respectively, which is close to the activation energy for vacancy migration. The authors of^[89] conclude that in polycrystals dislocation climb is accelerated by the motion of vacancies along dislocations from grain boundaries to jogs, and that this process governs the kinetics of climb. It should be noted, however, that in^[89] the activation energy ~ 47 –48 kcal/g-atom was obtained experimentally for polycrystalline Cu at 700°C, and that the mechanical treatment of polycrystals was followed by annealing for 30 minutes at

650°C. Single crystals were, of course, not subjected to mechanical treatment. We can therefore not exclude the possibility that small values of Q in polycrystals at 400–500° are partially associated with the results of cold working that are not removed at relatively low-temperature annealing.

The activation energy for nonsteady-state creep was also determined in [88]. The value 49 kcal/g-atom obtained for polycrystals coincides with the activation energy for self-diffusion.

The different stages of isothermal creep (nonsteady-state and steady-state with $\sigma < \sigma'$ and $\sigma > \sigma'$) were interpreted in [88] by considering the participation of different dislocations (edge and screw dislocations) with jogs in causing the different stages of creep, and the relative effectiveness of the obstacles blocking dislocations in each stage (Lomer barriers, dislocational walls of subgrains, and grain boundaries). The authors regard the exponential dependence of V on σ as basic and deny reality to the power law in Weertman's theory. The principal indirect argument is the following. When the creep isotherms $V(\sigma)$ obtained for Cu at 400–700° are represented by Weertman's equation, non-integer and nonconstant values of the exponent n are obtained, varying from 3 to 6, to which it is difficult to attribute any physical meaning. It must also be noted, however, that in [88] a nonconstant value of γ was obtained in the exponential formula (5), depending on temperature according to the law $\gamma = \gamma_0 \exp(-E/kT)$, where $E = 7.0$ kcal/g-atom. The value of γ thus varies by $1\frac{1}{2}$ orders of magnitude within the investigated temperature range.

The authors of [88] believe that the exponential form of $V(\sigma)$ for steady-state creep is entirely compatible with the climb mechanism. Considering a model of creep in which jogs are held up by obstacles, which can be circumvented only by climb of the jogs, semi-qualitative calculations lead to an exponential dependence of V on σ with reasonable parameters.

Although insufficient experimental data on steady-state creep are available at the present (extremely little data on alloys, no relationship established in many publications between the observed laws or constants and the original state of specimens etc.), we can assume that at any medium temperatures this process is actually governed by climb. Clarification of the details will require the improvement and development of the theory, together with much more experimental work. First of all, a careful determination of the form of $V(\sigma)$ will be required, agreeing with all known facts. It is also extremely important to account for the observed ranges of Q and n (when V is given as a power of σ) or of γ (for the exponential function). It appears that a complete and correct solution cannot be obtained without taking into account the previous history of specimens (cold working, annealing etc.) on creep kinetics at different temperatures.

III. LOAD-ENDURANCE INTERVAL (LONG-TIME STRENGTH)

The rapid increase in the number of different uses of various construction materials under the most diversified conditions has in the last two decades led to the discovery of hitherto unknown laws of fracture. One of the most important results* is the establishment of the way in which fracture strength depends on the duration of loading (in long-time strength). For each applied load bodies exhibit a definite load-endurance interval (duration in the unfractured state). The quantitative relationships determined in different foreign [52] and Soviet publications have been thoroughly investigated by S. N. Zhurkov and his co-workers. [53,54] According to [54] for the most diversified materials (metals, alloys, plastics etc.) the load-endurance interval τ depends on the applied stress σ and absolute temperature T according to a single law

$$\tau = \tau_0 \exp\left(\frac{U_0 - \gamma\sigma}{kT}\right), \quad (6)$$

where the constants τ_0 , U_0 , and γ are defined as follows: [54] U_0 is the activation energy for a local process developing with time under the load and leading to fracture, γ is the "activation volume," and τ_0 is of the order 10^{-11} – 10^{-12} sec (close to the period of thermal atomic oscillations in solids). [54] When (6) was fitted to the experimental results, U_0 exceeded the activation energy for self-diffusion by about 30% and reached the value of the latent heat of vaporization.

We note that (6) includes as a special case the "sudden" fracture of bodies when the critical stress is reached. As $T \rightarrow 0$, τ becomes $+\infty$ when $\sigma < U_0/\gamma$, and equals 0 when $\sigma > U_0/\gamma$. Thus the value $\sigma = \sigma_1 = U_0/\gamma$ is critical for $T \rightarrow 0$. When $\sigma < \sigma_1$ a body will remain unfractured for an indefinite period; when $\sigma > \sigma_1$ fracture occurs suddenly. On the other hand, Eq. (6) is not entirely consistent, since for $\sigma = 0$ (and $T \neq 0$) it yields a finite endurance interval, which implies the spontaneous fracture of bodies not subject to external forces.

It has been shown by direct experiments that when a body is subjected to a stress σ during a time τ_1 less than τ , followed by removal of the stress, recovery and reloading with the same stress σ , then fracture ensues at a time τ_2 after the second loading such that $\tau_1 + \tau_2 = \tau$. This proves that a continuous process in a loaded body produces irreversible changes, the accumulation of which leads to fracture. It should be noted, however, that if a body is heated to a high temperature during the nonloaded period, it is found experimentally [55] that changes are reversed and $\tau_1 + \tau_2 > \tau$. After a sufficiently long period at high temperatures, changes occurring during the first loaded period are completely reversed and we have $\tau_2 = \tau$.

The changes occurring in loaded bodies and leading

*For other pertinent effects see [50].

to fracture are of great fundamental interest. The exponential factor $\exp(U_0/kT)$ in (6) shows that thermal fluctuations are involved in the changes. Fracture results from the growth of cracks* of Griffith's "critical size." These are cracks whose growth reduces the elastic energy of the system more rapidly than the simultaneous increase of surface energy. It is thus reasonable to assume that in a stressed body the already existing or generated microcracks grow to the critical size under the given stress.†

Different mechanisms of crack growth can exist at different temperatures, even though the growth process always involves thermal fluctuations. At high temperatures the mechanism can be purely diffusional, while at medium temperatures thermally activated dislocation motion can also be involved. The purely diffusional model of crack growth was developed in [57]. It was postulated there that small incipient cracks (besides those due to inhomogeneities or imperfections) can result from vacancy clusters and can expand under a load. The stress concentration generated on the edges of cracks considerably reduces the activation energy required to add vacancies to a crack. In this way microcracks can grow at an appreciable rate even at not very high temperatures. Diffusional crack growth will not occur in an unloaded body at the same temperatures, because intensified stresses no longer reduce the activation energy.

The accumulation of vacancies in flat layers perpendicular to the direction of extension (crack formation and growth) reduces the elastic energy. Also, no work is required to increase the surface energy, since bonds between atoms lying on crack surfaces have already been broken as vacancies were formed. This process will therefore be "spontaneous" and can be observed experimentally under certain conditions.

For example, [78] in electrolytic metallic films having a very imperfect structure and reduced density heating results in processes of lattice "healing" (re-

gions having a regular crystal structure appear). The observation of low-angle x-ray scattering also shows that "submicroporosity" is produced. Excess vacancies unite as the lattice is healed to form submicropores. With increasing temperature the submicroporosity grows to a maximum, after which it decreases practically to zero (as a result of sintering, i.e., the removal of pores by diffusion). This represents an approach to thermodynamic equilibrium of the body. Under tension, however, processes induced by heating develop in an entirely different manner. Submicroporosity not only does not decrease at very high temperatures but increases strongly with applied stress. In an elongated body a near-equilibrium state includes pores similar in shape to microcracks. After high-temperature annealing under a load the cracks become large enough to be seen through a microscope.

We have thus found that cracks form and grow spontaneously in a stressed body. The resulting state is nearer to equilibrium than in the absence of cracks.

The direct observation of the foregoing effect is, of course, possible only for special objects such as electrolytic metallic films, due to the large excess of vacancies created at high temperatures. There can be no doubt that similar processes also occur in ordinary cast metals and alloys as cracks of critical size are generated.

Considering that the effective mean stress at the edge of a crack is increased by a factor $\sim \lambda/\delta$ (λ is the crack length and δ is the atomic diameter) and that $\lambda = \delta\sqrt{n}$, where n is the number of vacancies uniting to form a crack, we can estimate the reduction of activation energy required to unite a neighboring vacancy to a crack. The result obtained is $\sigma\delta^3\sqrt{n}$. It must also be remembered that the joining of a vacancy to a crack means that an atom lying at the edge of a crack moves deeper into the crystal. The elastic energy of the volume element occupied by this atom is then reduced by $\sigma^2\delta^3/2E$, [57] where E is the elastic modulus. In the inverse process the energy of the system would increase by the same amount. An elementary calculation of the kinetics of pure diffusional crack growth, with the foregoing considerations taken into account, yields the following formula: [57]

$$\tau = C \frac{(kT)^2 E}{\sigma^3 \delta^4 D} \exp\left(-\frac{\sigma \delta^3 \sqrt{n_0}}{kT}\right), \quad (7)$$

where C is a constant of the order of unity and D is the self-diffusion coefficient. $D = D_0 \exp(-U_0/kT)$, where U_0 is the activation energy for self-diffusion and n_0 is the number of vacancies forming the initial incipient crack. Equation (7) differs from (6) by the pre-exponential factor, which makes τ infinite when $\sigma = 0$ and $T \neq 0$. The same factor also contains $(kT)^2$. Therefore when (7) is fitted to experimental data (over a broad temperature range) the value obtained for the activation energy of fracture differs from the result obtained by means of (6). [54] It has been found [58]

*Fracture through the growth of cracks also applies to the case of so-called local brittle fracture, even when this is accompanied by plastic deformation near the site of the fracture. Other forms of fracture in metals and alloys are also known, particularly the fibrous structure on the fracture surface, where the separation of two parts of a body proceeds through the extreme local elongation of individual fibers as a result of large local plastic deformation. Here the breaking of each fiber results from extreme local elongation that reduces the cross section to zero, as in the breaking of very viscous liquid filaments. The fibrous structure of a fracture surface represents "viscous" fracture, [56] which will not be discussed in the present article.

†The growth of macroscopic cracks is sometimes accompanied by plastic deformation in a layer of some thickness (less than crack length) adjacent to the crack surface. In this case, in addition to an increase of surface energy, work is done to produce plastic deformation. The critical crack size now depends on the stress according to the formula [92] (see also [36]) $\sigma\sqrt{\lambda} \cong \sqrt{Ep}$, where p is the specific work of plastic deformation when $p \gg \alpha$. When α cannot be neglected compared with p , we have the formula $\sigma\sqrt{\lambda} \cong \sqrt{E(p+\alpha)}$. [83]

that the available measurements, including those given in [53,54], are consistent with an activation energy that is practically equal to the activation energy for self-diffusion. The value of n_0 is found to be of the order 10^3 , corresponding to incipient cracks having an initial length $\sim 10^{-6}$ cm.

In recent studies the initiation and growth of cracks in stressed bodies have been considered from the point of view of dislocation theory. In most cases the details of the thermally activated process have been omitted, and thermal activation has been treated purely formally by including the exponential factor $\exp(-U_0/kT)$. The initial hypothesis of this treatment is that there can be no stable existence of microcracks in solids without a dislocation mechanism. An initiated crack should close up spontaneously with the formation of a prismatic dislocation, since the elastic energy of the dislocation will be smaller than the surface energy of the crack. It is estimated in [75] that a thin stable planar crack in a plastic crystal can attain a length of the order 10^{-7} – 10^{-6} cm, and can reach 10^{-5} cm only in special cases. It must be noted that this and similar estimates pertain to an ideal crystal containing no imperfections other than the given crack or a prismatic dislocation resulting from the closing of the crack. It is easily seen that when any irregularities exist near a crack, such as atomic clusters in interstices or other edge dislocations, the elastic energy of the system can be elevated much more by the closing of the crack than has been assumed in the aforementioned calculation. Therefore a stable crack is considerably lengthened.* All dislocation schemes of crack generation and growth essentially use, in some form or other, the idea that some assembly of dislocations leads to the generation and stable growth of cracks. Stroh's model [36] is often used as a basis. Here, when an array of parallel dislocations is piled up at an obstacle, the high stress field created around the leading dislocation can induce the creation and propagation of a crack to some distance with the speed of sound. The weakness of this model is the difficulty of indicating the specific obstacles that immobilize a leading dislocation and that are able to maintain very high stress concentrations (except possibly when the obstacle is a grain boundary).

In [59] the aforementioned model is the basis of a schematic account of non-diffusional crack growth accompanied by considerable plastic deformation (Fig. 4). It is here suggested that piled-up dislocations enter a developing crack; this leads to a reduction of the stress blocking the dislocation source feeding the given slip

*It must also be kept in mind that in the initial stage of crack collapse the total crystal energy will not be reduced, but will increase since the surface energy remains practically unchanged while the elastic energy increases. This means that the two states of the body—with a collapsed (closed-up) and uncollapsed crack, respectively—are separated by a potential barrier that rises even higher when a tensile stress is applied to the body.

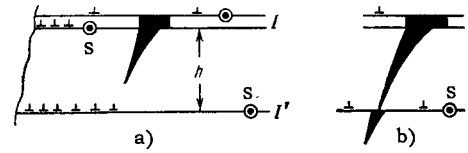


FIG. 4. Propagation of a crack.[59]

plane, and the source emits additional dislocations. It is also assumed that since the wide end and tip of a crack are subject to a tensile stress, crack growth by a fluctuation mechanism becomes possible. A crack can then grow by a series of jumps; in each jump a redistribution of stresses occurs in the slip plane supplying the crack with dislocations, and additional dislocations enter the crack. When the tip of a crack reaches the next slip plane (Fig. 4) it enters a compressed region of the crystal and the growth of the crack is decelerated. It is assumed that the crack tip can pass through the next slip plane abruptly, after which propagation of the crack in the extended crystal region becomes easier, while the part of the crack on the other side of the slip plane closes. The second slip plane is then in the same state that existed in the first slip plane when the crack opened up; the process continues in this manner. A crack propagating through a crystal leaves a trail in the form of microcracks alternating with dense regions, thus weakening a cross section of the crystal. Since during the propagation of a crack blocked dislocation sources are reactivated and begin to emit new dislocations, the growth of a crack must be accompanied by plastic deformation. A computation in [59] shows that on this model the product of the load-endurance interval τ and the deformation rate V is constant ($V\tau = 10^{-1}$), in agreement with certain experimental data on metals.[54] It is assumed that

$$V = l'\nu_0 \exp\left(-\frac{U_0 - \gamma\sigma}{kT}\right), \text{ where } \nu_0 \text{ is the frequency}$$

of lattice vibrations and l' is the mean distance between obstacles, the surmounting of which determines the velocity of crack propagation. Although this is a thermally activated process, U_0 was not computed but was assumed to have the excessive value given in [54] without the aforementioned pre-exponential factor.

In [60] a different calculation, based on a dislocation mechanism, takes into account the energetic advantage of crack opening. It is here assumed that stresses are concentrated in a layer of thickness $l \sim 10^{-6}$ cm between grains of a polycrystal with grain diameters $d \gg l$. Following the relaxation of stresses, slip and the concentration of elastic energy in the given layer produce the higher stress $\sigma_1 = \sigma\sqrt{d/l}$ in the latter. It is shown that the opening of a crack is favored energetically only when $\sigma > E(\delta/d)^{3/4}$, where E is the elastic modulus.* When $\sigma > E\sqrt{\delta/d}$ the stress at the wide end of a crack exceeds the theoretical strength, and in an ideal elastic body a crack should develop with

*The surface tension is estimated to be $\alpha \sim E\delta$.

the velocity of sound. When σ is between the limits $E(\delta/d)^{3/4} < \sigma < E(\delta/d)^{1/2}$ crack growth through thermal fluctuations is possible at a slow rate. Crack growth is favored energetically, but since the stress is subcritical thermal fluctuations are necessary for the growth. In [60] crack growth is regarded as caused by intensified stresses with thermal fluctuations aiding the successive local breaking of bonds between atoms, thus overcoming the "theoretical" strength. The load-endurance interval is given by the formula

$$\tau = \tau_0 \exp\left(\frac{U_0 - \gamma\sigma}{kT}\right), \quad (8)$$

which is taken to agree with the experimental results given in [53,54]. However, the authors of [60] disregard the fact that the calculation of τ_0 gave

$$\tau_0 = \frac{2}{\nu_0} \left(\frac{kT}{\sigma\delta^3}\right)^2 e^{-\beta}, \quad (8a)$$

where β is a constant and ν_0 is the period of lattice vibrations, i.e., that the pre-exponential factor contains $(kT)^2$. The activation energy of the fracture process determined experimentally from (8) or (8a) will not coincide with the latent heat of vaporization, as was found in [53,54].

A positive result achieved in [60] is the relationship established between γ and d : $\gamma = \delta^3 \sqrt{d}/\delta$, i.e., $\gamma \sim \sqrt{d}$, thus confirming the experimental data on the endurance interval of metals and alloys with different grain sizes. [61] This result appears to follow from the hypothesis that stresses are concentrated in layers. A similar relation between fracture strength (in short-time static tests) and grain size follows from Stroh's model (on the hypothesis that dislocations are stopped at grain boundaries) and is confirmed experimentally. [80,84] We note that [60] considers neither the specific dislocation mechanism causing stresses nor the form of thermal fluctuations. Comparative activation energies are not calculated for the proposed and other fluctuation processes. When a crack develops with the breaking of interatomic bonds, only a small fraction of bonds between each atom and its neighbors will be affected and we would expect the activation energy to be considerably smaller than the latent heat of vaporization per atom, which corresponds to the breaking of all bonds. In this case the activation energy will also not coincide with the activation energy for self-diffusion.

More accurate information is needed regarding the temperature and stress ranges in which the fracture mechanism of [60] is valid. The same applies to the other fracture mechanisms mentioned above.

Although there is no doubt that at low temperatures cracks are generated and grow through some dislocation mechanism aided by thermal fluctuations, additional understanding of this mechanism is still required. Decisive information would be obtained by direct observation, as in an electron microscope, of

effects produced by dislocation interactions and crack formation.

Up to the present time several interesting observations have resulted from the use of optical microscopes, although only relatively large cracks have been detected. In [90-92] the development of pores and cracks at a copper bicrystal boundary has been investigated under shear stresses applied parallel to the boundary. It was found that the area of pores and cracks relative to the boundary area is proportional to slip deformation along the boundary (displacement of the two parts of the bicrystal). The proportionality coefficient is independent of the experimental temperature (650-900°C). The authors assume that this observation excludes the possibility of pore and crack formation through vacancy condensation. They relate pores and cracks to the existence of boundary jogs existing originally or resulting from plastic deformation in the halves of the bicrystal. (Slip along crystallographic planes inclined with respect to the boundary is understood.) The last explanation was advanced in [94]. However, since slip along grain boundaries is known to depend exponentially on the reciprocal of temperature* for a given applied stress, the same temperature dependence is obtained from the results in [91-93] for a relative area of pores and cracks that does not exclude the possibility of a vacancy mechanism. In [91-93] no quantitative data are given regarding the temperature dependence of slip on a bicrystal boundary, nor the dependence of slip on the relative orientation of bicrystal grains (halves). The microscopic pattern of deformation in the grains was not investigated.

Important microscopic observations of crack formation have been reported for deformed zinc single crystals. Thus Gilman observed cracks in Zn slip planes (which are here also cleavage planes) that cannot be attributed to piled-up dislocations since a pile-up produces zero normal stress on a slip plane. In the model proposed to account for this effect a crack represents the break in a vertical dislocational wall (perpendicular to a slip plane) when a part of the wall is immobilized by an obstacle, such as a sub-grain boundary, while the remainder of the wall is moved by an applied stress.

The explanation of crack development in stressed bodies is aided by the observation of the behavior of bodies in the presence of absorptionally active media that reduce the surface tension and thus increase crack size. In a microscopic investigation of crack development in amalgamated zinc crystals, Rozhanskiĭ [94,95] studied the bending of slip planes, as a result of which a dislocation pile-up easily generates

*Slip on grain boundaries is related linearly to creep elongation. [97] According to [98] the relative displacement of the grains on the boundary results principally from unequal grain deformation on both sides of the boundary.

cracks at the tip of the pile-up itself (as in Gilman's mechanism) rather than ahead of the pile-up (as calculated by Stroh). According to Rozhanskiĭ's observations such cracks formed in nearly parallel slip planes are easily joined, resulting in crystal fracture. The calculation of the conditions for crack formation in a slip plane, with slip developing along bent planes, was given recently by Indenbom,^[98] who also considered other mechanisms of crack formation.

Kochanova et al^[77] reports an investigation of cracks in differently oriented amalgamated zinc crystals with different elongations. It was concluded that a crack results initially from deformational inhomogeneities (incomplete shearing or dislocation clusters), i.e., the applied cleavage stress plays the principal role. When the effective normal stress becomes so large that the crack becomes unstable and able to grow by the Griffith mechanism, the second stage of crack development begins and leads rapidly to fracture. The same article contains an investigation of cleavage through the brittle fracture of amalgamated zinc single crystals. The observed pattern was interpreted using ideas regarding the dominant role of edge or screw dislocations in the formation of cleavage cracks. These conclusions have still not been extended to the temperature-velocity dependence of brittle fracture, like the aforementioned results of other microscopic investigations.

With regard to the macroscopic laws greatest interest attaches to a comparison of experiment with the pre-exponential factor in the formula for τ , since the same exponential expression applies formally to the different models and mechanisms. Experiment shows^[47] that in many metals $\ln \tau + 3 \ln \sigma$ at medium and high temperatures depends linearly on σ (Fig. 5), which corresponds to a diffusional mechanism of crack growth. We must note, however, that the dislocational theory of long-time strength has still not been perfected to take dislocation climb into account. The experimentally observed relation $\ln(\tau\sigma^3) \sim A\sigma$ is a possibility here.

Evidence supporting the diffusional mechanism of

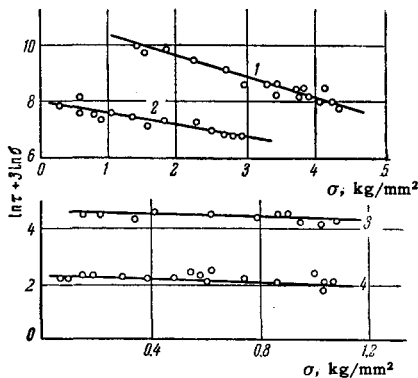


FIG. 5. Dependence of $\ln \tau + 3 \ln \sigma$ on stress σ for Cu and Ni specimens.^[47] 1 - Ni, 900°; 2 - Ni, 1100°; 3 - Cu, 900°; 4 - Cu, 1040°.

crack growth at medium and high temperatures is provided by measurements of the load-endurance interval performed on cold-worked or electrolytic specimens (i.e., in an initially nonequilibrium state). The data of^[62] shown in Fig. 6 reveal the longest endurance interval at high temperatures in annealed specimens, which are closest to thermodynamic equilibrium.

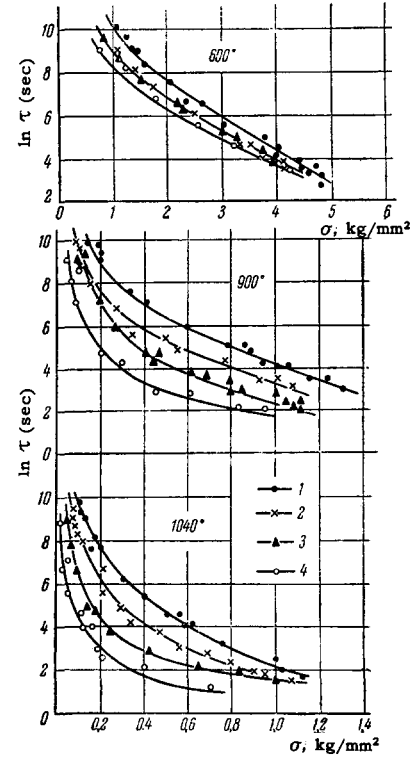


FIG. 6. Dependence of $\ln \tau$ on σ for Cu specimens at different temperatures.^[62] 1 - annealed specimens; 2 - 20% deformed specimens (at room temperature); 3 - 50% deformed specimens; 4 - electrolytic specimens.

Fracture strength (and the endurance interval) are reduced in cold-worked and especially in electrolytic specimens, where at medium and high temperatures, as is well known, all diffusion processes are accelerated as a large number of excess vacancies appear with "healing" of the lattice. On the other hand, at temperatures where the dislocational mechanism of delayed fracture is active, we can expect an enhanced interval and fracture strength following cold working.

IV. DIFFUSIONAL CREEP

J. I. Frenkel was the first to point out^[42] that at high temperatures external forces can induce permanent deformation in solids through "viscous flow" similar to the flow of a viscous fluid and resulting from successive random motions of individual atoms, i.e., by diffusion processes. This kind of deformation should occur under any small, nonvanishing, applied stress and is thus characterized by the absence of a yield point, which is always associated with deforma-

tions depending on dislocation motion. Deformation resulting from viscous flow does not produce hardening and will progress at a constant velocity V proportional to the applied stress: $V = \sigma/\eta$, where η is the coefficient of viscosity. In viscous flow the shape of a body can change without affecting its crystalline structure; therefore its behavior under external forces should be unchanged, independently of any preceding deformation. The foregoing pertains only to bodies in a state of thermodynamic equilibrium or to bodies in which such equilibrium is established very rapidly. In practice, crystalline bodies heated to the high temperatures at which viscous flow can occur always have a previous history involving lattice defects that influence the viscous flow. It is important that at high temperatures the "healing" of nonequilibrium effects occurs as well as an approach to thermodynamic equilibrium. Frenkel developed the concept of viscous flow as applied to the sintering observed at high temperatures in pressed crystalline powders, where deformation results in viscous flow under capillary forces. It must be emphasized that, according to Frenkel, a diffusion mechanism provides the basis for viscous flow. This is seen from the relation between the coefficients of viscosity and self-diffusion:

$$\frac{1}{\eta} = \frac{D\delta^3}{kTL^2}, \quad (9)$$

where L is some characteristic dimension of the body. Equation (9) is very general and is derived from the differential equations of viscous flow and diffusion, independently of the kind of stressed state. In the given form it applies to crystals; a similar relation $1/\eta = D\delta/kT$ for liquid (or amorphous) bodies is obtained from (9) by substituting $L = \delta$.

Unfortunately, the literature, especially the technical literature,^[63] reveals a large amount of confusion about this topic. Different theories of sintering, based on ideas regarding bulk diffusion, vacancy migration etc., are regarded as independent of each other although they do not differ essentially from the Frenkel theory of sintering. It has been stated that the existence of a large number of different sintering theories results from the great complexity of the effect, which can thus not be described by a single theory. In actuality the principal process involved in sintering is diffusional creep (which Frenkel called viscous flow). The effects that accompany sintering (recrystallization, diffusion along grain boundaries, evaporation and condensation from the gaseous phase, heterodiffusion in multicomponent systems etc.), like sintering itself, are processes wherein the system approaches thermodynamic equilibrium and are realized through a diffusion mechanism or similar effects resulting from thermal fluctuations. The laws of sintering are discussed elsewhere;^[44] we wish only to point out that in real cases these laws are complicated by the departure of crystal lattices from thermodynamic equilibrium

in grains of dispersed powders during sintering. This is shown mainly by the greater velocity of diffusion processes resulting from a large number of excess vacancies and by the gradual decrease of this velocity as thermodynamic equilibrium is approached.

The experimental investigation of diffusional creep (viscous flow) by observing sintering is difficult because it is impossible to exclude the influence of capillary forces during heating, when the state of a body changes as it approaches equilibrium. There is therefore great interest in the experiments where viscous flow is observed (in cast metals and alloys, and cermets) under external forces. These experiments have given us a more detailed understanding of the basic character of pure diffusional creep at high temperatures.

Diffusional creep in polycrystalline metals, for example, outwardly resembles creep resulting from the motion or climb of dislocations. In this case changes in the creep rate are also divided into three stages: 1) unsteady decreasing creep, 2) steady-state creep, and 3) accelerated creep ending in fracture. (These stages have a greatly different origin than for dislocational creep.) The first stage depends entirely on the initial nonequilibrium of these specimens. After pre-annealing at high temperatures the first stage disappears completely (Fig. 7). Creep from the instant of loading then occurs at a constant rate, which in well-annealed specimens is strictly proportional to the applied stress, as is to be expected from the Frenkel theory of viscous flow. An enhanced but diminishing creep rate in the first stage of unannealed specimens clearly results from the increased velocity of the diffusion process, probably caused by the excess vacancies that appear when lattice defects are "healed." The first stage of diffusional creep can be induced artificially by cold working of well-annealed specimens (Fig. 8). It is interesting that diffusional and dislocational creep exhibit opposite effects induced

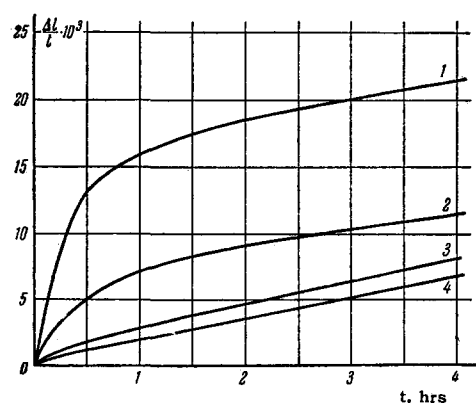


FIG. 7. Creep (elongation $\Delta l/l$ vs. time t) at 1000°C under the load $\sigma = 10 \text{ g/mm}^2$ in Cu specimens pre-annealed at 1000°C for different periods. 1 - $\theta = 0$; 2 - $\theta = 15 \text{ min}$; 3 - $\theta = 1 \text{ hr}$; 4 - $\theta = 4 \text{ hrs}$.^[50]

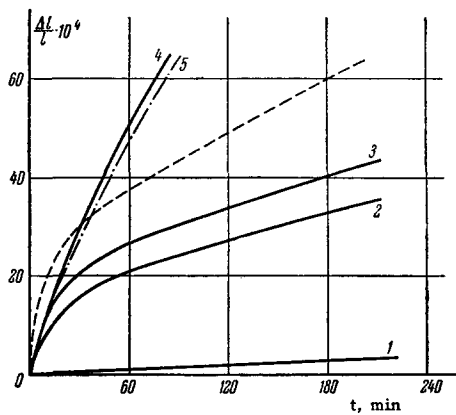


FIG. 8. Dependence of $\Delta l/l$ on time t for creep in Fe.^[64] 1 – at 900°C after heating to 1250°; 2 – at 900° after heating to 1250° plus 2% deformation at room temperature; 3 – at 900° after heating to 1250° plus 10% deformation at room temperature; 4 – at 1200° after heating to 1250° plus 10% deformation at room temperature; 5 – at 1200° after heating to 1250°. The dashed curve is given for a specimen tested at 900° without pre-annealing. In all cases $\sigma = 100 \text{ g/mm}^2$.

by cold-working and annealing. After cold-working, dislocational creep diminishes in the first stage while diffusional creep is enhanced.^[64] On the other hand, after an anneal dislocational creep is enhanced in the first stage while diffusional creep, as already noted, disappears.

Processes that increase the vacancy concentration (leading away from equilibrium) must accelerate diffusional creep, especially in the first stage. Thus in a nonhomogeneous system of grains of interdiffusing metals (such as pressed mixtures of Ni and Cu powders), where heating induces unequal partial heterodiffusion accompanied by the creation of very many excess vacancies, a very sharply pronounced stage of diffusional creep is observed.^[50]

It should be noted that in crystals with several different indications of nonequilibrium, specifically in metals and alloys with lattice distortions, inhomogeneous composition, porosity etc., external forces applied at high temperatures induce various diffusion processes by which thermodynamic equilibrium is approached through an identical vacancy mechanism. The rates of such processes depend on the simultaneous occurrence of other processes. Specifically, acceleration recovery under load is observed. During creep there is a more rapid deceleration of sintering, heterodiffusion etc. because of the more rapid removal of excess vacancies participating in creep.^[65]

Thus the experimental investigations of diffusional creep at high temperatures have revealed several "nonequilibrium" effects governing the behavior of bodies and determining how viscous flow changes the conditions for the approach of a system to equilibrium.

It must be mentioned that until a system has reached complete equilibrium the observed laws of creep differ from the expected behavior. Thus in the case of in-

complete equilibrium the steady-state creep rate is proportional to σ^k with $k \sim 1.3-1.5$; $k = 1$ only in well-annealed specimens. The self-diffusion coefficient $D = D_0 \exp(-U_0/kT)$ calculated from data on η is also too large; the activation energy U_0 is too small and only in extremely well-annealed specimens attains a value consistent with that determined directly in self-diffusion experiments.^[50,64]

In addition to the nonequilibrium effects that distinguish creep in crystalline bodies from creep in amorphous (or liquid) bodies a specific effect in crystal deformation by diffusional creep must be mentioned; this is the so-called "aftereffect." At the unloading of a specimen subjected to high-temperature creep, deformation of reversed sign is observed^[66] having a value π depending on the stress and temperature at which creep takes place. The following laws have been observed to govern the aftereffect deformation π . At a given temperature π is proportional to the rate of preceding creep; this is independent of whether the creep rate changed under an applied stress of different magnitude, or through pre-annealing that brought the specimens near thermodynamic equilibrium in experiments where the applied stress remained constant (Fig. 9). When the applied stress remains constant and temperature varies (along with the creep rate, which increases with temperature) the observed aftereffect is reduced as the temperature increases (and

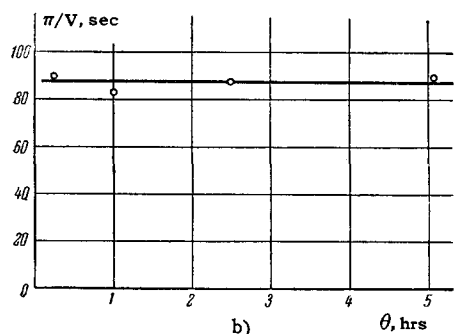
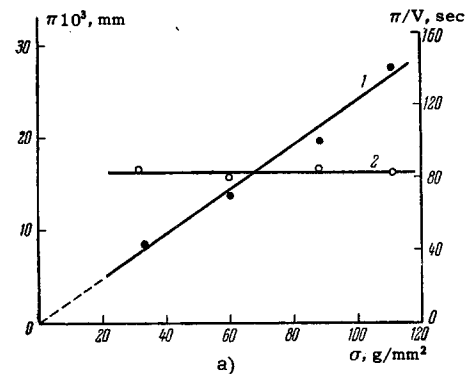


FIG. 9. a) Dependence of the reverse aftereffect π (1) and ratio π/V (where V is the creep rate) (2) on stress σ in Cu at 850°C, for four stresses: 32, 61, 89, and 111 g/mm^2 .^[66] b) π/V as a function of the duration θ of pre-annealing at 1040°C. Tested at 850°C, $\sigma = 30 \text{ g/mm}^2$.^[66]

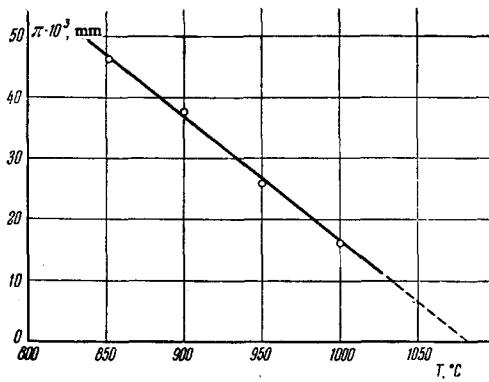


FIG. 10. Temperature dependence of the reverse aftereffect π in Cu ($\sigma = 30 \text{ g/mm}^2$, at 850, 900, 950, and 1000°C).^[66]

approaches zero at the melting point—Fig. 10). If with changing temperature the load is such as to maintain the creep rate, the observed aftereffect deformation is proportional to the load (Fig. 11). The ratio of π to deformational creep Δl approaches unity for $\Delta l \rightarrow 0$ and then decreases, at first extremely rapidly and then more slowly (Fig. 12). These laws agree with the interpretation of the diffusional mechanism of creep in a uniformly stressed state,^[68] according to

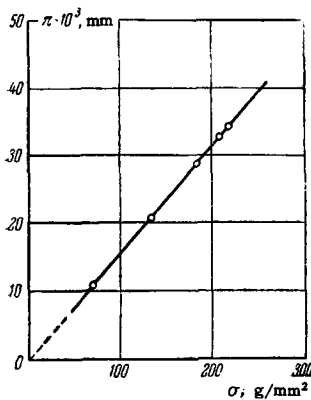


FIG. 11. Dependence of π on stress σ in Cu. (for $V = \text{const}$)^[66]

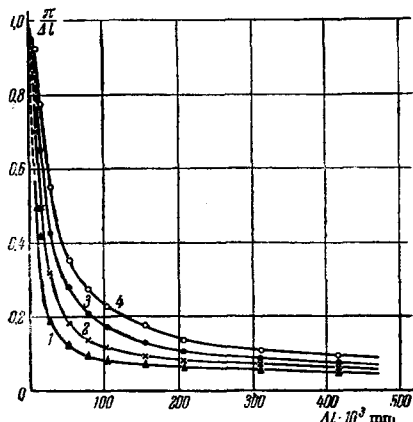


FIG. 12. Dependence of the ratio $\pi/\Delta l$ on creep deformation at constant temperature (900°C) for different stresses. 1 – 25, 2 – 50, 3 – 100, 4 – 150 g/mm^2 .^[66]

which elongation after creep deformation under tensile stress proceeds gradually through atomic diffusion that fills extra atomic planes located between the fundamental crystal planes perpendicular to the direction of tensile loading. The extra planes are built up out of atoms departing from the lateral surfaces of the specimen. During the initial stage of creep elongation the applied stress first produces two-dimensional nuclei of new planes, which are in most cases extremely unstable. Release of the applied stress is sufficient to cause ‘resorption’ of these nuclei by diffusion. With a considerable development of creep elongation the relative number of these nuclei decreases sharply at first, and later more slowly. Nuclei attaining macroscopic dimensions (having areas of the same order as the cross-sectional area of a grain) will remain after unloading. However, an applied stress continually generates new relatively unstable nuclei whose ‘resorption’ at unloading causes the aftereffect.

There is considerable interest in the experimental study of creep at high temperatures in single crystals and brittle crystalline bodies, where it is easy to observe directly the structural changes accompanying deformation. Such investigations are still few in number. In ^[67] creep was studied in the elongation of brittle crystalline specimens of aluminum (flat ribbons 2.5 mm thick) having $\sim 3.3\text{-mm}$ mean grain size in the plane of the ribbon. The experiments were conducted near the melting temperature (at 920°K or 647°C); the stress varied from 2.24 to 28.5 g/mm^2 (2.8–36.55 lb/in^2). An almost constant creep rate was observed at each stress (Fig. 13). At the lowest applied stresses the specimen was compressed instead of being extended; this is accounted for by surface tension, which makes a specimen tend to become equidimensional through reduction of its length. These experiments were performed in air and the specimen was covered with a thin oxide film, so that the effect resulted from the surface tension of Al_2O_3 and the interphase surface tension at the $\text{Al}\text{-Al}_2\text{O}_3$ boundary. The dependence of the creep rate V on stress is shown in Fig. 14. $V > 0$ beginning at 3.2 g/mm^2 ; up to 10.4

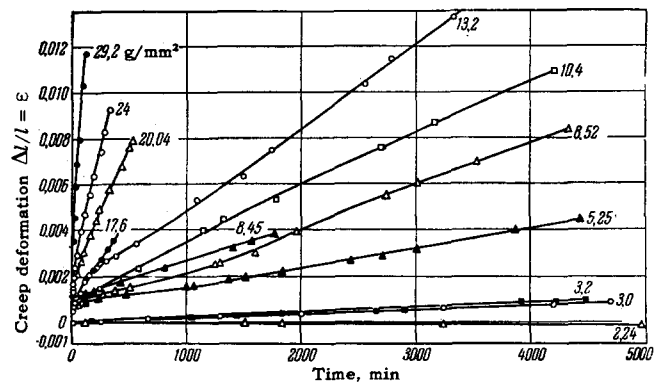


FIG. 13. Creep in high-purity Al at 920°K (647°C) at stresses from 2.24 to 28.5 g/mm^2 .^[67]

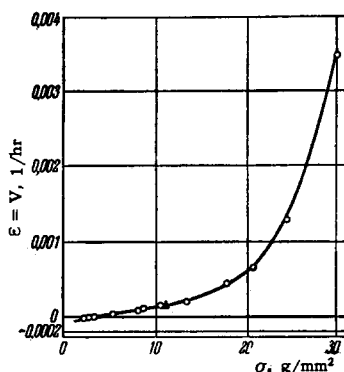


FIG. 14. Dependence of creep rate V on stress σ in high-purity Al at 647°C.^[67]

g/mm^2 V depended linearly on the stress σ . At higher stresses V increased approximately as the fourth power of σ . By observing the change of the creep rate at a sudden temperature rise the activation energy $U_0 = 35.5$ kcal/g-mole was determined; this value agrees with the activation energy of self-diffusion in aluminum. U_0 was found to be independent of the stress. Following deformation under 8 g/mm^2 at 647°C a Laue pattern exhibited no asterism; thus the deformation produced no structural changes that could be detected by x-ray study. The oxidation of the surface prevented a microscopic observation of slip traces. The observed creep rate under low stresses ($\sigma < 10.4 \text{ g/mm}^2$) was compared with the formula

$$V = \frac{10}{3} \left(\frac{4\pi}{3L^3} \right)^{2/3} \frac{ND\delta^3\sigma}{RT}, \quad (10)$$

based on Herring's model, where L is the grain size, R is the gas constant, N is Avogadro's number, δ^3 is the atomic volume, and D is the self-diffusion coefficient; the experimental creep rate was about three times as large as the calculated value. It was concluded therefrom that despite the agreement of low-stress effects with what is expected for viscous flow, the observed creep under low stresses at a high temperature is not caused by viscous flow. This conclusion was confirmed by control experiments on creep in an aluminum single crystal at 647°C under 7.2 g/mm^2 , where deformational creep of the same magnitude as in the polycrystal was observed. According to Herring's theory^[69] (see below) diffusional creep results from the existence of grain boundaries and should not occur in a single crystal. These control experiments also produced a disagreement with Herring's theory because of the fact that a polycrystalline specimen will be lengthened uniformly (with no dominant lengthening near grain boundaries). Finally, one of the arguments against the viscous origin of high-temperature creep is the existence of the aftereffect (a deformation of opposite sign after unloading), which was also observed.

The experimental data in ^[67] are of great interest, but the given interpretation appears to be based on

several confusions. We first note those connected with Herring's theory, according to which diffusional creep in a polycrystal subjected to pure shear develops as the atomic chemical potential at grain boundaries changes under an applied stress. The magnitude of this change is $\sigma_{\perp}\delta^3$, where δ^3 is the atomic volume and σ_{\perp} is the normal stress at the boundary. At stressed boundaries the chemical potential is reduced, while at compressed boundaries the potential is increased; the former boundaries are sinks for atoms while the latter are sources. The existence of sources and sinks at grain boundaries produces gradients of the chemical potential and diffusion currents of atoms within grains from compressed to stretched boundaries (Fig. 15). The grains will therefore be shortened in the direction of compression, and will be lengthened in the direction of stretching. New layers of atoms diffusing from the compressed boundaries should grow near stretched boundaries.

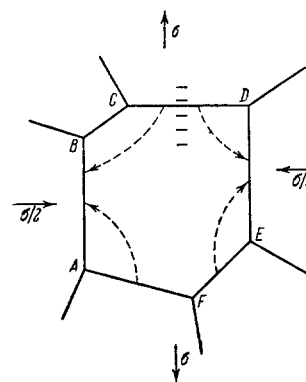


FIG. 15.

Herring's theory is not exhaustive and is incomplete in many respects. This theory neglects the interphase surface energy at grain boundaries, which can differ at the different boundaries, and fails to take into account the possible increase of this energy as grain shapes change. Other neglected effects are associated with the nonuniform flow of atoms along boundary surfaces and with the gradual growth of new atomic layers parallel to the boundaries.* It is not determined under what conditions a boundary becomes a source or a sink; the minimum angle of misfit between neighboring grains must be known for this purpose. Also, the theory considers only the growth of new atomic layers near stretched grain boundaries and fails to consider the possibility that new atomic planes can be built up between the original planes within the grains (far from the boundaries). Equation (10), which relates the creep rate to the stress σ , is correct to within a numerical coefficient independently of the specific model of diffusional creep. This equation does not differ essentially from (9) and is obtained, as already indicated, in a very general way from the equations of diffusion

*These effects cause the "aftereffect."

and viscous flow. According to this formula the creep rate in both single crystals and polycrystals in [67] should be identical, since this rate is practically determined by some minimum linear dimension of the specimens. In [67] this dimension was the ribbon thickness 2.55 mm, which in the polycrystalline specimens was smaller than the other linear grain dimensions (~ 3.3 mm). We note that in Herring's theory creep can be associated with exterior as well as with interior grain boundaries, all of which can be sources or sinks for atoms. Therefore the foregoing conclusion does not at all conflict with Herring's theory.

Another source of misunderstanding in [67] was the neglect of nonequilibrium states remaining even at near-melting temperatures in insufficiently well-annealed specimens. In [67] this is manifested by the retention of a small region of nonsteady-state creep, and also by the excess of the observed creep rate above the calculated rate. (This difference is very small in [67].) In other investigations, such as [70], the discrepancies were limited to only one order of magnitude, which cannot be regarded as an essential contradiction considering the qualitative character of the theoretical values.* Another adverse feature in [67] was the impossibility of investigating surfaces microscopically because of oxidation. This made it impossible to compare the surface state following deformation under low stress, corresponding to viscous flow, with the state under high stresses, when the observed dependence of V on σ agrees with Weertman's prediction in connection with the dislocation climb mechanism.

In [71] structural changes were investigated following creep in copper single crystals at 1050°C , near the melting point. It was found that these structural changes differ considerably under low stresses ($< 30\text{--}50$ g/mm² in the given case) and high stresses. With the latter, slip traces (Fig. 16) appear on the surface and Laue patterns exhibit asterism. On the other hand, following deformation of the same magnitude (up to 10%) under low stresses slip traces are entirely absent, while the spots in Laue patterns become clearer and sharper instead of exhibiting asterism. It should be noted that slip traces following deformation at such high temperatures can be observed only from the "steps" on an untreated surface. Slip traces cannot be observed following polishing and etching, unlike the case for low-temperature deformation. It is seen that dislocations whose movements produce slip traces under high stresses are rapidly "resorbed" at the high temperature. We also note that following creep deformation at high temperatures and low stresses the surface of a copper single crystal exhibits a peculiar effect (Fig. 17)—grooves 15μ deep at right angles to the direction of elongation (independently of the crystallographic orientation of the specimen). These

*Herring in [69] points out the approximate character of the theoretical results.

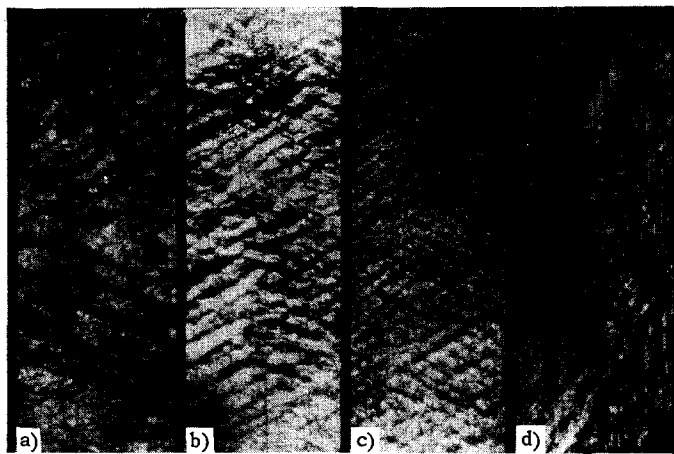


FIG. 16. Slip traces following high-temperature creep in Cu single crystals [71] at 1050°C . $10\times$. a) $\sigma = 100$ g/mm², duration of stretching $\theta = 6$ hrs, $\epsilon = 20\%$; b) $\sigma = 200$ g/mm², $\theta = 6$ min, $\epsilon = 10\%$; c) $\sigma = 560$ g/mm², $\theta = 1$ min, $\epsilon = 40\%$. In a), b), and c) the direction of elongation was close to [100]. d) $\sigma = 200$ g/mm², $\theta = 2$ hrs, $\epsilon = 10\%$, direction [110].

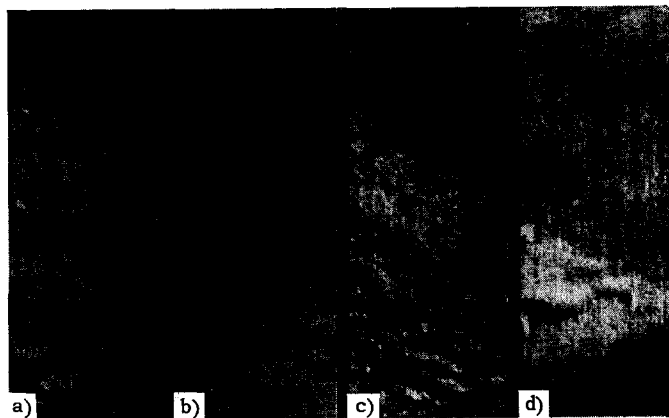


FIG. 17. Development of transverse grooves with high-temperature (1050°C) creep in Cu single crystals. [71] $10\times$. a) $\sigma = 20$ g/mm², duration of stretching $\theta = 45$ hrs, $\epsilon = 10\%$; b) $\sigma = 25$ g/mm², $\theta = 28$ hrs, $\epsilon = 7\%$; c) $\sigma = 30$ g/mm², $\theta = 35$ hrs, $\epsilon = 10\%$; d) $\sigma = 15$ g/mm², $\theta = 50$ hrs, $\epsilon = 3\%$.

grooves appear to result from the nonuniform migration of surface atoms to the interior during diffusional creep. This can be explained easily.

The thermal fluctuation required to remove a surface atom adjoining a vacancy (left by a previously migrating atom) is smaller than for an atom all of whose neighbors remain fixed. Once atomic migration from any surface region has begun, the process will continue to develop there in preference to other regions. Some part in the formation of grooves can also possibly be played by local inhomogeneities. In [71] it was desired to determine whether the absence of slip traces following low-stress deformation can be attributed to the duration of a high temperature when a large deformation is achieved, which requires a correspondingly long period under a load. For this pur-

pose specimens exhibiting slip traces under high stresses were annealed further (25–30 hrs) at the same temperature (1050°C) at which they were deformed. This anneal produced no change in the pattern of slip traces accompanying deformation. This contradicts the hypothesis that deformation under small loads also results from slip, but that the slip traces are eliminated during a long period at high temperatures. At small stresses and high temperatures deformation is evidently purely diffusional and corresponds to viscous flow. The characteristics of deformation are associated here with the successive building up of atomic layers and with the possible existence, even at near-melting temperatures, of the residual effects of nonequilibrium states accelerating diffusion processes.

Recent observations of diffusional creep in nonmetals deserve to be mentioned. An investigation of very pure porefree aluminum oxide at 1400–1800°C showed^[100] an increase of the creep rate with diminishing grain size d . The investigation was quantitative for grain sizes 6–36 μ , and qualitative for the range 60–125 μ because it was difficult to measure the slow creep rate accurately. This result was opposite to that expected in the case of dislocational creep. The high purity of the specimens and the relatively small decrease of their fracture strength at the given high temperatures guaranteed that the effect did not result from softening of amorphous layers at grain boundaries, which often occurs in ordinary ceramic materials of technical purity. The creep rate V was found to depend linearly on the stress σ and to be inversely proportional to the square of grain diameter d :

$$V \sim \frac{\sigma}{d^2}. \quad (10a)$$

At the same time, single crystals of Al_2O_3 (sapphire) at 1400–1500°C exhibited creep deformation only at higher stresses, with $V \sim \sigma^m$, where $m \sim 4$. Creep is here apparently of dislocational origin and is possibly associated with dislocation climb.

Using (10a) and Herring's formula $V \sim 10D\delta^3\sigma/(d/2)^2kT$ (with δ^3 representing the volume of oxygen atoms or ions in the Al_2O_3 lattice) the author of^[100] determined the partial self-diffusion coefficient $D(T)$ of oxygen in Al_2O_3 from the experimental creep rate. The result agreed well with that obtained by calculating the kinetics of the intermediate and final sintering stages. However, the result is several orders larger than the directly measured oxygen diffusion coefficient in Al_2O_3 as given in the literature (the discrepancy is about two orders of magnitude for polycrystals and about four orders for single crystals). The lattice of sintered Al_2O_3 evidently still possesses excess defects.

The results in^[100] show that in nonmetals, because of the great difficulty of achieving crystallographic slip, the effects of diffusional creep can appear at temperatures considerably farther from the melting point than in the case of metals.

Interesting observations of crack formation on grain boundaries perpendicular to the tensile stress are also reported in^[100]. Pores and cracks appear not only at the junctions of several grains, but also in the middle of flat grain boundaries, whence they spread over entire boundaries.

The foregoing discussion shows that certain published doubts regarding the governing role of diffusion in high-temperature creep (and sometimes a doubt regarding the very existence of diffusional creep in crystals) are not justified, and that they result from an oversimplified treatment neglecting complications arising from the existence and preservation of nonequilibrium crystal states up to near-melting temperatures. On the other hand, there can be no doubt that insufficient experimental study has been made of pure diffusional creep in single crystals having different degrees of lattice perfection. A complete understanding of diffusional creep in solids will require experimental investigations of all aspects.

We now conclude our short review of the mechanical properties of solids associated with diffusion processes. This has not been an exhaustive account, if only because it has been confined to one-phase and one-component objects. Great practical importance attaches to diffusion processes under applied stresses and resulting from deformation in inhomogeneous bodies, such as the decomposition of solid solutions, various phase transitions, recrystallization etc. This is too broad a subject and has not been well developed quantitatively, although much practical information has been accumulated and is used in technology for different kinds of thermal and mechanical-thermal treatments. In the case of one-component bodies no questions connected with recrystallization during deformation, phase transitions etc. were treated. The entire foregoing discussion shows the great influence of diffusion processes on mechanical properties at high and medium temperatures. A basis for understanding this influence has undoubtedly been provided by Frenkel through his concepts of the diffusion mechanism by means of vacancy migration, and of vacancy generation by the movement of atoms to interstices. These concepts combined with the atomic models developed in dislocation theory form a basis for understanding and interpreting the variety of mechanical properties of solids at medium and high temperatures. Other contributions by Frenkel to the theory of mechanical properties include the development (in collaboration with T. A. Kontorova) of a statistical theory of the brittle fracture of real crystals,^[72] the theory of the stability of incipient cracks,^[73] the theory of the mechanical properties of glass,^[74] the aforementioned theory of "caterpillar" motion of dislocations,^[25] and others.^[99] These achievements of Frenkel have not been discussed here in detail since they lie outside the scope of this review. With his ideas regarding diffusion and his theory of viscous flow in

solids, which have been discussed here, Frenkel made a fundamental contribution to science that will long continue to aid in accounting for the complex mechanical properties of solids at medium and high temperatures.

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