

RECRYSTALLIZATION AND GRAIN GROWTH

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METALS HAVE been worked and annealed since prehistoric times, but little attempt was made to explain the changes that occur during annealing until 1881, when KALISHER¹ observed that heating caused changes in the 'molecular structure' of cold-worked zinc. By then it was well known that metals are crystalline, and Kalisher assumed that the working destroyed the crystallinity of the metal, and that heating permitted it to recrystallize. From that time there has been a continuous series of papers describing, explaining and formulating the

changes that occur during annealing. The results of the very early workers have been summarized by CZOCHRALSKI² and later reviews have been written by SCHMID and BOAS,³ SACHS and VAN HORN,⁴ BURGERS,⁵ MEHL⁶ and BURKE.⁷

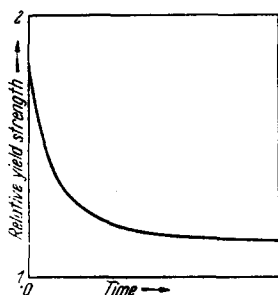


Figure 1. Isothermal recovery curve (schematic)

Terminology

The annealing process is complex and a deformed metal may pass through a number of stages while it is being restored to essentially perfect crystallinity. It has been customary

to apply the terms recovery, recrystallization and grain growth to these stages. These terms, however, have carried different connotations of mechanism and driving force to different workers, so that it is often difficult to know which to apply to a given transformation. We shall use these terms with approximately their common meanings, but shall redefine them to permit their use with less ambiguity.

Recovery—This is the first change that occurs upon annealing a deformed metal. We shall apply the term to the essentially continuous changes in physical properties that occur in the unrecrystallized part of a deformed metal during annealing. Recovery has no incubation period and the rate decreases as the process proceeds, as shown in the typical recovery isotherm of *Figure 1*. It is intended that this definition should include the process of polygonization⁸ but not the restoration of physical properties by the migration of grain boundaries which were

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present prior to deformation. This latter process we consider to be grain growth.

Recrystallization—The recrystallization of a deformed metal resembles a phase transformation, in that it can be described in terms of a nucleation frequency \dot{N} and a linear rate of growth G . After an incubation period, strain-free grains start to grow from a number of sites, the number of sites increases with time, and the strain-free grains grow until they have consumed the matrix. A graph of the fraction transformed as a function of time gives a sigmoidal reaction curve as shown in Figure 2. We shall consider recrystallization to be that transformation which occurs in a cold-worked metal with reaction kinetics of this type. It should be noted that this definition makes no assumption about the nature of recrystallization nuclei or about the mechanism of their formation. Part of the process may be identical to grain growth.

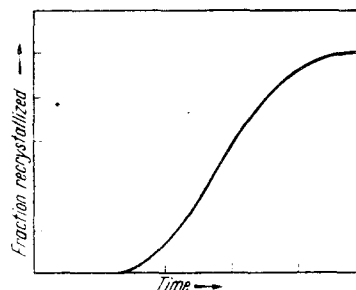


Figure 2. Isothermal recrystallization curve (schematic)

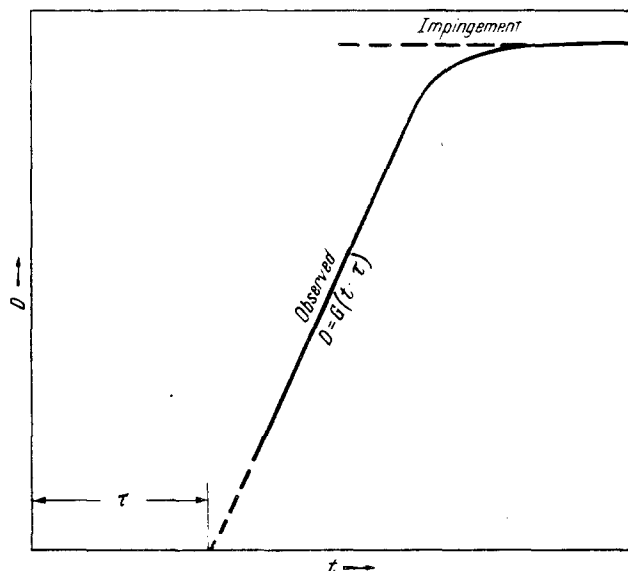


Figure 3. Size, D , of recrystallized grain as a function of time (schematic)

A process which is kinetically identical may occur under special conditions in a metal that has already undergone recrystallization. The term 'secondary recrystallization' has been applied to the process,

and because it can be described in terms of N and G we shall also use this term. Since prior deformation does not seem to be required for secondary recrystallization, it will be considered to be a special case of grain growth. Where it is necessary to avoid ambiguity, the term 'primary recrystallization' will be applied to recrystallization in a deformed metal.

Grain Growth—Grain growth occurs by the migration of grain boundaries that were present prior to annealing. It can occur in deformed specimens, but the term will be taken specifically to refer to the increase in grain size that results from annealing after recrystallization is complete. No reaction kinetics are specified for grain growth, and they may vary with the material. In an undeformed metal, if the grain size remains uniform, the rate of grain growth decreases as the grain size increases. During secondary recrystallization, the rate of growth is independent of time.

'Laws of Recrystallization'

By about 1920, the effects of a number of variables upon recrystallization and grain growth had been established qualitatively. These are usually presented as the laws of recrystallization. Briefly, these 'laws' are as follows:

- 1 a minimum deformation is necessary to cause recrystallization
- 2 the smaller the degree of deformation, the higher is the temperature required to cause recrystallization
- 3 increasing the annealing time decreases the temperature necessary for recrystallization
- 4 the final grain size depends chiefly upon the degree of deformation, and to a lesser extent on the annealing temperature, being smaller the greater the degree of deformation and the lower the annealing temperature
- 5 the larger the original grain size, the greater is the amount of cold deformation required to give equivalent recrystallization temperature and time
- 6 the amount of cold work required to give equivalent deformational hardening increases with increasing temperature of working
- 7 continued heating after recrystallization is complete causes the grain size to increase.

Where the quantities of interest are primarily a suitable temperature for annealing and the grain size that will result from annealing, the above laws give a satisfactory qualitative statement of the effect of variables on the process. A more quantitative description of the

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process, however, requires a more detailed statement of the kinetics, and the atomic mechanisms by which the cold-worked metal is restored through annealing. We shall here consider the process from these standpoints.

Energies Involved

Since the transformations which occur during annealing will be considered largely from the point of view of energy, it is interesting to review the magnitude of the energies involved.

TAYLOR and QUINNEY⁹ have measured calorimetrically the heat evolved on annealing cold-worked metals and find it to be of the order of 0.5 to 1.0 cal/gm, or for copper about 30 cal/gm atomic weight. Part of this energy will be evolved during recovery and part during recrystallization. During grain growth after recrystallization, the energies are an order of magnitude smaller. Assuming the grains are close-packed cubes the grain boundary area per cubic centimetre equals $3/D$ cm² where D is the grain diameter in centimetres. SEARS¹⁰ finds the specific surface energy of grain boundaries to be about 500 ergs or approximately 10^{-5} cal/cm². Thus, for a grain size of 10^{-3} cm, the grain boundary energy is about 0.21 cal/gm atom for copper. If the grain diameter increases by a factor of ten, about 0.19 cal/gm atom will be evolved. These values may be compared with 3,100 cal/gm atom for fusion of copper.

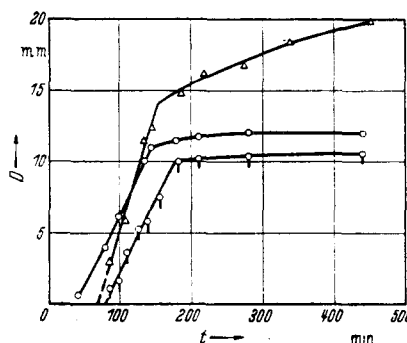


Figure 4. D as a function of time for three grains in the recrystallization of fine-grained aluminium

FORMAL THEORY OF RECRYSTALLIZATION KINETICS

Description of Nucleation and Growth—Microstructural observations have shown that the progress of isothermal recrystallization can be described, under certain conditions, in terms of the parameters \dot{N} , nucleation frequency and G , the linear rate of grain growth. Let a dimension of a grain growing isothermally into a strained matrix be D . Then it is frequently observed¹¹⁻¹³ that D varies with time, t , as shown schematically in Figure 3. From the time that the recrystallizing grain becomes distinguishable from the surrounding matrix until it impinges upon other recrystallizing grains or the specimen boundaries, D is generally described by the relation:

$$D = G(t - \tau) \quad \dots (1)$$

where $\tau \geq 0$, G is the linear rate of growth, and τ is the nucleation period. The average τ is reciprocally related to the nucleation frequency,* \dot{N} . Description of the entire observable process of recrystallization requires the integration of the relations of the type shown in equation 1 in three dimensions for all the recrystallizing grains and the solution of the geometrical problem of impingement.

Let the total volume of substance be unity and X the volume (or fraction) recrystallized in time t . It is required to find $X = f(t)$. A derivation will be given that follows those of VON GÖLER and SACHS,¹⁴ JOHNSON and MEHL¹⁵ and AVRAMI (now MELVIN)¹⁶ for general nucleation growth processes. Let G_x , G_y and G_z be linear growth vectors for the x , y and z directions. Then neglecting impingement the volume v of a particular recrystallized grain at time t is:

$$v = fG_x G_y G_z (t - \tau)^3 \quad (2)$$

where the growth vectors are assumed to be independent of time and f is a shape factor. If \dot{N} is the nucleation frequency per unit volume the number of grains dn originating in a time interval $d\tau$ is:

$$dn = \dot{N}(1 - X) d\tau_{t=\tau} \quad (3)$$

In the von-Göler-Sachs treatment an unimpinged volume X' is evaluated from the relation

$$X' = \int_0^t v dn = fG_x G_y G_z \int_0^t (t - \tau)^3 \dot{N}(1 - X) d\tau_{t=\tau} \quad (4)$$

and X' is assumed equal to X . Because it does not take impingement into account, the von-Göler-Sachs equation can only be strictly applicable when $X \rightarrow 0$. In the Johnson-Mehl and Avrami derivations a number dn' is defined as follows:

$$dn' = dn + \dot{N}X d\tau = \dot{N}d\tau \quad (5)$$

where $\dot{N}X d\tau$ is the number of 'phantom' grains that would have originated in the volume X had it not recrystallized. The extended volume X_{ex} calculated without regard for impingement and counting the phantoms is given by:

$$X_{ex} = \int_0^t v dn' = fG_x G_y G_z \int_0^t (t - \tau)^3 \dot{N} d\tau \quad (6)$$

To complete the solution of the problem an equation relating X_{ex} and X is needed. Johnson and Mehl, and Avrami have written the necessary relation as follows:

$$dX/dX_{ex} = 1 - X \quad (7)$$

* The word nucleation implies no particular mechanism but is applied to a process whose kinetics are partly described in terms of the parameter τ .

Any perimeter laid down at random on a cross section consisting of transformed and untransformed material will intersect untransformed material along $1 - X$ of its total length. Since the increment of the total length of the perimeter of all grains, intersecting a cross section including phantoms (to ensure complete randomness) is proportional to dX_{ex} equation 7 follows. A more rigorous derivation¹⁶ has been given by Avrami.

Substituting equation 7 into equation 6 gives the basic relation common to the Johnson-Mehl and Avrami theories as follows:

$$\int_0^X dX/(1 - X) = -\ln(1 - X) = fG_x G_y G_z \int_0^t (t - \tau)^3 \dot{N} d\tau$$

. . . . (8)

or

$$X = 1 - \exp\left(-\int_0^t v dn'\right)$$

. . . . (9)

In the recrystallization of thin sheets it may happen that the lateral dimensions of the recrystallized grains become much larger than the sheet thickness δ so that the value for v to be used in solving equation 9 is

$$v = fG_x G_y \delta (t - \tau)^2$$

. . . . (10)

rather than equation 2 that holds for 'three dimensional' recrystallization. Similarly in the recrystallization of thin wires of diameter δ , where the length of the recrystallized grains is much larger than δ , the expression for v is

$$v = fG_y \delta^2 (t - \tau)$$

. . . . (11)

Essentially the Johnson-Mehl and Avrami treatments diverge only in their assumptions on the form of the function $\dot{N} = f(\tau)$ to be used in the solution of equation 9. According to the Johnson-Mehl theory the function must, in general,* be evaluated by experiment while Avrami assumes an explicit form for it. According to Avrami's theory there are pre-existing in the untransformed matrix a limited number \bar{N} of preferred nucleation sites each having a nucleation frequency ν . In ordinary phase transitions these sites may be occupied by inclusions that happen to catalyse the formation of nuclei of the new-forming phase. In recrystallization reactions positions where the strain is extraordinarily large may be the preferred nucleation sites. At any rate during recrystallization the sites are used up by becoming recrystallization nuclei and the number of potential nucleation sites N remaining after time τ is:

$$N = \bar{N} \exp[-\nu\tau]$$

. . . . (12)

giving

$$\dot{N} = \bar{N}\nu \exp[-\nu\tau]$$

. . . . (13)

* Johnson and Mehl did make some assumptions about the form of $\dot{N} = f(\tau)$ for the purpose of showing how equation 9 might be solved to give simple relations in specific instances.

PROGRESS IN METAL PHYSICS

Substituting in equation 9 and letting $G_x = G_y = G_z$ gives:

$$X = 1 - \exp \left\{ -\bar{N} \nu f G^3 \int_0^t (t - \tau)^3 \exp[-\nu \tau] d\tau \right\} \quad \dots (14)$$

and upon performing the integration:

$$X = 1 - \exp \{ (\sigma f G^3 \bar{N} / \nu^3) [\exp(-\nu t) - 1 + (\nu t) - (\nu t)^2/2! + (\nu t)^3/3!] \} \quad \dots (15)$$

For νt very large this approximates to*:

$$X = 1 - \exp[-f G^3 \bar{N} t^3] \quad \dots (16)$$

while for $\nu t \rightarrow 0$

$$X = 1 - \exp[-f G^3 \bar{N} \nu t^4/4] \quad \dots (17)$$

Equation 17 is formally the same as obtained by Johnson and Mehl when $\dot{N}(= \bar{N}\nu)$ was assumed to be independent of time and $G_x = G_y = G_z$. Avrami proposes that for three dimensional recrystallization in general:

$$X = 1 - \exp[-Bt^k] \quad \dots (18)$$

with

$$3 \leq k \leq 4$$

By substituting equations 10 or 11 in equation 9 and carrying out the indicated operations, it can be verified that equation 18 holds also for two dimensional recrystallization with

$$2 \leq k \leq 3$$

and for one dimensional recrystallization with

$$1 \leq k \leq 2$$

Table I summarizes some limiting equations obtained from the Johnson-Mehl and Avrami theories.

Table I. Limiting Equations obtained from the Johnson-Mehl and Avrami Theories

Type of Recrystallization	$X = f(t)$	
	Johnson-Mehl assuming $\dot{N} = \text{constant}$	Avrami k values in $X = 1 - \exp(-Bt^k)$
Three dimensional	$X = 1 - \exp(-fG^3\dot{N}t^4/4)$	$3 \leq k \leq 4$
Two dimensional (e.g. sheet) . .	$X = 1 - \exp(-fG^2\dot{N}t^3/3)$	$2 \leq k \leq 3$
One dimensional (e.g. wire) . .	$X = 1 - \exp(-fG\dot{N}t^2/2)$	$1 \leq k \leq 2$

* When νt is very large N equation 12 $\rightarrow 0$ in a time that is very short relative to the time at which $X = 1/2$.

Although Avrami's theory is very flexible, as it stands it requires that \dot{N} always decreases or remains essentially constant with time and makes no provision for the experimental facts (to be described in a following section) that \dot{N} sometimes increases sharply with time. In describing this behaviour the Johnson-Mehl theory, that makes no assumption about $\dot{N} = f(\tau)$, is more flexible.

Some Alternative Descriptions of Recrystallization Kinetics—KRUPKOWSKI and BALICKI¹⁷ have proposed that recrystallization is a first order reaction so that:

$$dX/dt = k(1 - X) \quad (19)$$

which when integrated with the condition $x = 0$ at $t = 0$ gives:

$$X = 1 - \exp[-kt] \quad (20)$$

The concept that recrystallization be described as a first order rate process is not compatible with the nucleation growth description unless the parameters \dot{N} , G decrease with time in an arbitrary manner. Apparently Krupkowski and Balicki envisage recrystallization as an essentially homogeneous process that can be treated in a manner analogous to the Bragg-Williams treatment¹⁸ of the kinetics of order-disorder reactions. Since the form of most recrystallization isotherms is sigmoidal (*Figure 2*), contrary to the predictions of equation 20, the description of recrystallization as a first order rate process cannot be generally valid.

COOK and RICHARDS¹⁹ also have proposed another description of recrystallization kinetics independent of the \dot{N} , G concept. They postulate that recovery is a first order rate process so that the fraction w of a specimen recovered in time t is:

$$w = 1 - \exp(-\beta t) \quad (21)$$

where β is a constant. They further postulate that the rate of recrystallization is a first order process confined entirely to the part of the specimen which has undergone recovery. It follows then that the rate of recrystallization is:

$$dX/dt = kw(1 - X) = k(1 - \exp[-\beta t])(1 - X) \quad (22)$$

where k is a constant.

Making the approximation

$$w = \beta t \quad (23)$$

valid only for $1 \gg w$, equation 22 was integrated to give

$$-\ln(1 - X) = (k\beta/2)t^2 = Ct^2 \quad (24)$$

Cook and Richards' equation 24 is identical in form with Avrami's equation 18 derived on the basis of the \dot{N} - G description for two dimensional growth. Should Cook and Richards' relation be found

applicable to a recrystallization process in which grains grew as polyhedra rather than as platelets the \dot{N} - G description could be satisfactory only if G decreased with time.

A basic assumption of the formal theory just presented, is that nucleation is equally probable in any volume element of the deformed specimen which is equal to or smaller than the minimum resolvable volume of the recrystallized grains. Data on recrystallization kinetics are probably not yet sufficiently extensive to require any more special assumptions for their description. However, a formal theory¹⁵ that treats the problem of preferential nucleation at grain boundaries has been given by Johnson and Mehl.

*Description of Experiments in Terms of Formal Recrystallization Theory—*KARNOP and SACHS¹¹ first proved the applicability of the \dot{N} - G description to recrystallization by their experiments on lightly deformed (9 to 10 per cent) fine-grained aluminium. Their technique consisted in measuring the grain size D of particular recrystallizing grains after various periods of time at the annealing temperature. However, in order to reveal the grain boundaries, it was necessary, after each period of time at the annealing temperature, to cool the specimen to room temperature and etch. Their results demonstrated that D for each recrystallizing grain was satisfactorily described (before impingement) by equation 1. Some of their data are plotted in *Figure 4*.

Using a similar technique KORNFIELD and PAVLOV¹³ confirmed the validity of the \dot{N} - G description in the recrystallization of fine-grained aluminium wires deformed 3 to 8 per cent in tension and investigated the effect of temperature, strain and prior recovery treatments on \dot{N} and G . KORNFIELD and SAWIZKI²⁰ showed that the recrystallization of polycrystalline tin, cadmium, and iron strained 2.0, 0.6 and 3.5 per cent, respectively, is satisfactorily described in terms of \dot{N} and G . Also, by using the cooling-etching technique, COLLINS and MATHEWSON²¹ proved that the recrystallization of heavily deformed high purity aluminium single crystals takes place by an \dot{N} - G process.

The experimental technique of Karnop and Sachs and Kornfeld and co-workers has been criticized on the following grounds²²:

- i* additional strains may be put into the specimen by heating and cooling the sample between room and the annealing temperature and by handling during etching
- ii* the etching treatment *per se* might modify the subsequent course of recrystallization.

A technique which circumvents these objections is that of viewing the progress of recrystallization through a window in the annealing furnace. This method is not often applicable to experiments on the recrystallization of metals because boundary migration progresses

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more rapidly than boundary grooves can develop by thermal etching. However, MÜLLER¹² observed that during the recrystallization of deformed rock salt single crystals, crystal boundaries were clearly delineated at all stages of their progress by the different reflectivity of crystal faces and by thermal etch pits. From the standpoint of precision, reproducibility and completeness of data on the effect of variables on \dot{N} and G , Müller's investigation stands as one of the most excellent in the field of recrystallization kinetics. His results prove that the recrystallization of rock salt crystals closely follows the \dot{N} - G description for strains (compression at 400°C) at least as large as 50 per cent.

The results that have been reviewed in the foregoing, show the validity of the \dot{N} - G description in recrystallization, but give no information on the applicability of the impingement theory. Some experiments of MEHL and co-workers²²⁻²⁴ were designed to test the impingement theory and to measure \dot{N} more quantitatively.

Mehl and his co-workers used a statistical procedure to measure \dot{N} and G that consists in annealing various equivalent samples for different periods of time and then measuring the number of grains and total progress of recrystallization in each. The size of the aggregate sample is chosen so that a large number of recrystallized grains have formed during the chosen time intervals. Thus statistical fluctuations in \dot{N} are small. G is determined by plotting the diameter of the largest unimpinged grain *versus* time and is assumed to be the same for all grains—an assumption making their description less than completely satisfactory for evidence will be cited which demonstrates that G varies widely for different recrystallizing grains. However, from their analysis G proved to be independent of time and \dot{N} was found to be related to τ (equation 8) by the equation:

$$\dot{N} = a \exp[b\tau] \quad (25)$$

where $\exp(b\tau) \gg a$ for all times of observation. According to equation 25 \dot{N} increases sharply with time. This result is at variance with the prediction of the Avrami theory that \dot{N} should decrease or remain constant with increasing time.

Substituting equation 25 into the general equation obtained by Johnson and Mehl for two dimensional transformations STANLEY and MEHL²² obtain

$$X = 1 - \exp[-(2\pi G^2 \delta a / b^2) (\exp \{bt\} / b - bt^2/2 - 1/b - t)] \quad (26)$$

Figure 5 compares the transformation curve calculated from equation 26 and the directly measured transformation curve for an isotherm obtained by Anderson and Mehl in the recrystallization of high purity

aluminium. The agreement is fair and deviations may possibly be explained by the orientation dependence of G in addition to the experimental uncertainties.

It has been demonstrated that the kinetics of secondary recrystallization of copper having a high degree of cube orientation²⁵ and of silver²⁶ are entirely analogous to the kinetics of primary recrystallization in lightly deformed specimens. D values for particular grains are satisfactorily described by equation 1. WARD²⁵ found that \dot{N} in the secondary recrystallization of OFHC copper increases sharply with time according to the relation²² (equation 25) found by Stanley and Mehl, $X = f(t)$ was found in both investigations to be satisfactorily described by equation 9.

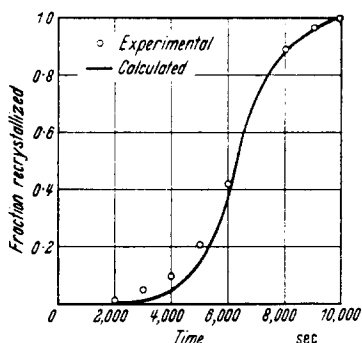


Figure 5. Comparison of experimental data with curve calculated from impingement theory for the recrystallization of aluminium: temperature = 350°C, $\epsilon = 0.051$

In some studies of isothermal recrystallization \dot{N} and G were not measured directly but certain observations were interpreted by making special assumptions about $\dot{N} = f(\tau)$, G as a function of orientation *etc.*

For example, Karnop and Sachs deformed a tapered (conical) specimen of electrolytic copper in tension to produce strains of 3 to 18 per cent along the length and annealed it for a definite period of time.¹¹ The strain at which the sample was estimated (by visual examination) to be approxi-

mately one half recrystallized and the size of the largest recrystallized grain in the region were recorded. The procedure was repeated for a sequence of times. G was calculated on the assumptions that it is independent of time and orientation and that $\tau = 0$ for the largest grain. \dot{N} was calculated from the Johnson-Mehl equation* (Table I) for three dimensional recrystallization on the assumption that it is independent of time. In view of later experiments, the validity of all the Karnop-Sachs assumptions with the exception that G is independent of time are open to serious question. Certainly, the results can give no clue on how the impingement problem should be described.

There seems to be no direct microstructural proof that the nucleation and growth picture of recrystallization can be extended to heavily deformed fine-grained specimens. Detailed information on the progress of microstructural changes during recrystallization can be obtained readily only when a marked contrast in size between recrystallized and

* Karnop and Sachs actually derived this equation but by an erroneous procedure. Von Göler and Sachs recognized the error and derived equation 4.

deformed grains develop. Such a contrast is observed in the recrystallization of single crystals or when a lightly deformed polycrystalline matrix recrystallizes to several grains, but no marked grain size contrast is observed when a heavily deformed polycrystalline matrix recrystallizes to a fine grain size. For these reasons, microstructural evidence on the applicability of the nucleation growth picture to the recrystallization of heavily deformed fine-grained specimens is difficult to obtain. However, it has been found in a number of instances that the progress of recrystallization in such specimens can be described by kinetic relations derived from the nucleation and growth picture.

DECKER and HARKER²⁷ and SEYMOUR and HARKER²⁸ have measured the progress of recrystallization in heavily cold-rolled (98 to 99.7 per cent) strips of copper²⁷ and nickel-iron alloy²⁸ by measuring the change of intensity of an appropriate Bragg reflection* from the rolled surface of a strip as a function of time at the annealing temperature. The intensity measurements were made with a Geiger counter x-ray spectrometer. Decker and Harker found that the recrystallization isotherms of spectroscopically pure copper were described by equation 18 with $k \simeq 3$. For OFHC copper $k \simeq 3$ for high temperatures and $k \simeq 2$ for lower temperatures. They interpret their results on the basis of the Avrami theory and suppose that $k \simeq 3$ when grains grow as polyhedra and $\simeq 2$ when grains grow as platelets (see k values for two and three dimensional recrystallization in *Table I*). This interpretation assumes that νt in equation 15 is very large or in different words that $\tau = 0$ for all grains. However, no microstructural evidence on how the grains actually grew was obtained. Alternative theories, also based on the \dot{N} - G picture, that explain their data as well are:

- I when $k = 3$ recrystallization is two dimensional, $\dot{N} \simeq$ constant and $G =$ constant
- II when $k = 2$ or 3 $\dot{N} \simeq$ constant but G decreases with time.

Cook and Richards have measured the isothermal rate of recrystallization of high purity copper rolled 80 to 98 per cent by following the change of hardness with time.¹⁹ The hardness change was related to the fraction recrystallized in several experiments by microstructural observations. They assert that their isotherms are satisfactorily described by equation 24 derived from their concept of a sequence of two homogeneous reactions (recovery and recrystallization), but note that equation 24 is identical in form with equation 18 derived for two dimensional recrystallization on the basis of the \dot{N} - G theory with $k = 2$. Also, an analysis of their results shows that $k \simeq 3 \pm 0.5$ at

* For example, the rate of appearance of the (200) reflection from planes perpendicular to the rolling direction.

50° and 2 ± 0.3 at 27°C in fair agreement with Decker and Harker. Even in the event that the recrystallization observed by Cook and Richards was three dimensional at the lowest temperature, it is possible that G decreases with time in such a way that $k \approx 2$. Thus, it appears probable that their results are consistent with the N - G picture and that it is unnecessary to invoke a two-stage homogeneous recovery and recrystallization sequence in order to explain them.

Effect of Variables on G

It has been pointed out that the N , G description is adequate for secondary recrystallization or discontinuous grain growth as well as

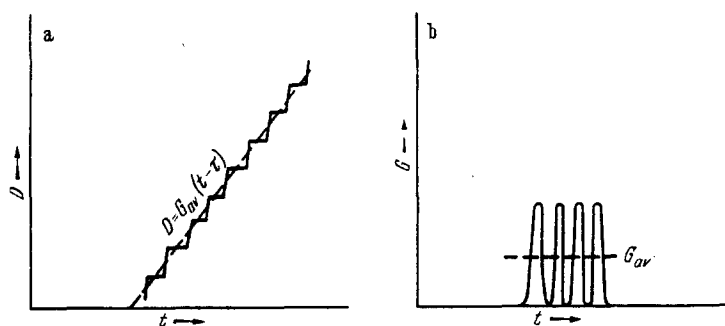


Figure 6. D and G as a function of time in the recrystallization of rock salt single crystals (schematic.)

for primary recrystallization processes. Also, there is good evidence that the kinetics of normal grain growth after completion of recrystallization are controlled in large part by a parameter G that is closely related to G values measured in primary and secondary recrystallization. For these reasons the effect of variables on G will be considered from a very general point of view and facts will be drawn from all types of processes in which G has been measured.

Time—It has been well established* that in the primary recrystallization of metals G is generally independent of time.^{11, 13, 21-24} Recent data^{25, 26, 29} have also confirmed the generalization for secondary recrystallization. However, interesting exceptions have been observed that merit serious consideration. Müller by his direct observation method found that G in the recrystallization of rock salt appeared to be independent of time in the low temperature range of his experiments.¹² However, in the high temperature range the boundary moved

* MEHL and co-workers^{25, 26} have critically surveyed the evidence bearing on these questions for metals.

in 'spurts' so that the relation of D and G to t is as represented schematically in *Figure 6*. During each period of rapid motion the boundary moves a distance $\alpha \sim 20$ to 30 microns. It is evident that the observed relation between D and t can be closely approximated by equation 1 with $G = G_{av}$. Nevertheless, G is clearly a periodic function of time and its maximum value may be almost an order of magnitude larger than G_{av} . Also BURKE³⁰ has observed that the motion of boundaries during the primary recrystallization of zinc at room temperature is jerky.

Since even in the event of jerky boundary motion the relation between D and t can be approximated by equation 1, the question must be raised whether the periodicity of G with time is a general phenomenon. Certainly the resolution of most of the experiments on metals^{11, 29} was not sufficient for any periodicity in G to be detected were δ the same order of magnitude as for rock salt. Further, a possible interpretation of Müller's failure to observe a periodicity of G in the low temperature recrystallization of rock salt is that $\delta \ll 1$ micron. Therefore, the significance and interpretation of G values measured in boundary migration experiments must be considered very carefully.

Occasionally it is observed that during recrystallization grains grow at a constant rate for a time and then practically stop growing before any impingement. Müller sometimes found this type of behaviour in the recrystallization of rock salt crystals containing 0.005 molecular per cent of strontium chloride as solute impurity. Similar phenomena have been observed in the secondary recrystallization of copper.³¹

Orientation—In general, G should be a function of relative grain orientations (specified by three parameters) and the boundary orientation (specified by two parameters). However, it appears that there are no completely quantitative data relating G to the orientation parameters though there is a large collection of qualitative data indicating that it is a sensitive function of them.

KORNFELD and RYBALKO³² observed marked growth anisotropy in the recrystallization of aluminium single crystals (99.5 per cent pure) elongated 12 to 18 per cent in tension. At 570°C the anisotropy in G was about six to one, but at higher temperatures it was much less pronounced.

The orientation of the new grains produced in the secondary recrystallization of cube-textured copper is frequently related to the orientation of the matrix by a rotation about a common (111) pole. BURKE and TURKALO³³ found that G for the new grains was greatest for growth in the [110] direction in the matrix which lies in the common (111) plane. In the [110] matrix direction 90 degrees away, G was several times smaller. Here again, the anisotropy was more pronounced at low than at high temperatures.

After the recrystallization of lightly deformed polycrystalline aluminium, very small crystals are often found embedded in the large recrystallized grains. Presumably these are unabsorbed crystals of the original matrix. TIEDEMA, MAY and BURGERS³⁴ have shown that the orientation of these occluded crystals is either very nearly identical or twin related to the recrystallized grain surrounding them. The interpretation is that G is very much smaller for such close orientation relations than for those where the orientations of the recrystallized grain and matrix are very different and not twin related.

BECK, SPERRY and HU³⁵ observed that, of several crystals formed by recrystallization around a scratch or pin prick in a lightly deformed

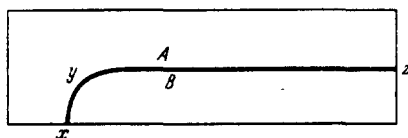


Figure 7. Schematic representation of technique proposed by Dunn³⁶ for measurement of grain boundary (xy) migration with a constant driving energy; crystal A grows at the expense of B

aluminium (single crystal) those related in orientation to the matrix grains by an approximately 30° rotation about a common $[111]$ pole grow several times faster than the crystals of other orientation relations formed around the scratch. These experiments further confirm the orientation dependence of G and have been

interpreted on the basis that the orientation relation for which G is a maximum always corresponds to the 30° rotation about the $[111]$ pole in face-centred cubic metals. It is possible that the wide variation in G for individual recrystallized grains growing in a deformed aluminium matrix, as observed in the experiments of KARNOP and SACHS,¹¹ and KORNFELD and PAVLOV¹³ for example, can be explained in terms of a relative grain and boundary orientation dependence.

Recently DUNN³⁶ has suggested an experimental technique whereby it should be possible to measure G quantitatively as a function of the orientation parameters. Figure 7 shows a specimen suitable for such measurements. Crystals A and B are prepared having a definite orientation relation by the technique worked out earlier by DUNN.³⁷ During the growth experiment boundary yz is consumed by the migration of boundary xy that retains a fixed curvature so that the driving force remains constant.

Temperature—For constant strain the dependence of G upon temperature has been described by the relation

$$G = G_0 \exp[-Q_G/RT] \quad (27)$$

Equation 27 is valuable only when there are extended ranges of temperature for which G_0 and Q_G are single valued. Actually in most experiments, where G has been measured in primary or secondary

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recrystallization, such extensive ranges of temperature have been revealed. Values of the constants G_0 and Q_G that satisfy equation 27 for various materials and strains are listed in *Table II*.

Also included in *Table II* are results of measurements on rates of normal grain growth. G in normal grain growth cannot have the same formal relation to atomic mobility as G in recrystallization. However, if it is supposed that the geometric sequence in normal grain growth is independent of temperature it follows that the difference in the relations is in the temperature independent factor. It may be assumed

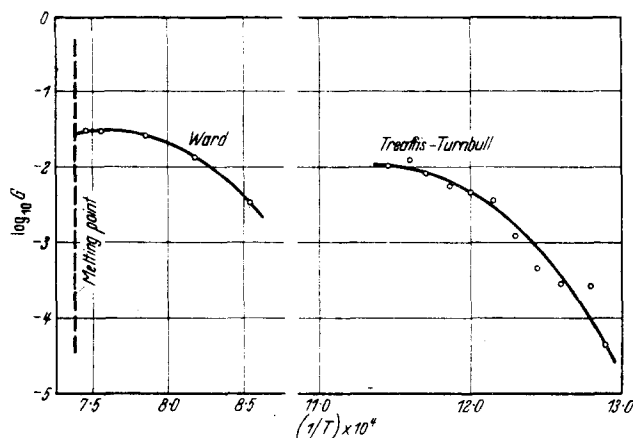


Figure 8. $\log G$ as a function of $1/T$ in the secondary recrystallization of OFHC copper and spectroscopically pure copper

that the temperature independent factor aG_0 for normal grain growth contains a geometric factor a (in general $a < 1$) that is not present in G_0 for recrystallization.

It is sometimes found that G for a particular metal and with an apparent constant driving energy is not described by a single value of Q_G over the entire temperature range of the measurements. In a number of instances Q_G was found to decrease with increasing temperature. Karnop and Sachs calculated¹¹ that Q_G decreased continually with increasing temperature in the primary recrystallization of copper and at 10 per cent strain ranged from 50 kcal/gm atom at 310°C to 32 kcal/gm atom at 350°C. Because of their assumptions, the results of Karnop and Sachs may be questioned, however, WARD²⁵ and later TREAFIS and TURNBULL³⁰ established by less questionable procedures that Q_G decreases sharply with increasing temperature in the secondary recrystallization of OFHC and spectroscopically pure copper, respectively. Figure 8 shows the relationship between $\log G$ and $1/T$ found in these investigations.

Anderson and Mehl report values²³ of G_0 and Q_G for the primary

recrystallization of aluminium that diverge widely from the values¹³ reported by Kornfeld and Pavlov for the recrystallization of aluminium wires at comparable strains (*Table II*). It is possible, of course, that this divergence may be attributed to factors such as purity, history, mode of deformation *etc.* However, a replot of the data of the two investigations on the same scale (*Figure 9*) reveals that the facts are also compatible with the interpretation that Q_G decreases with increasing temperature in the recrystallization of aluminium. For it is possible

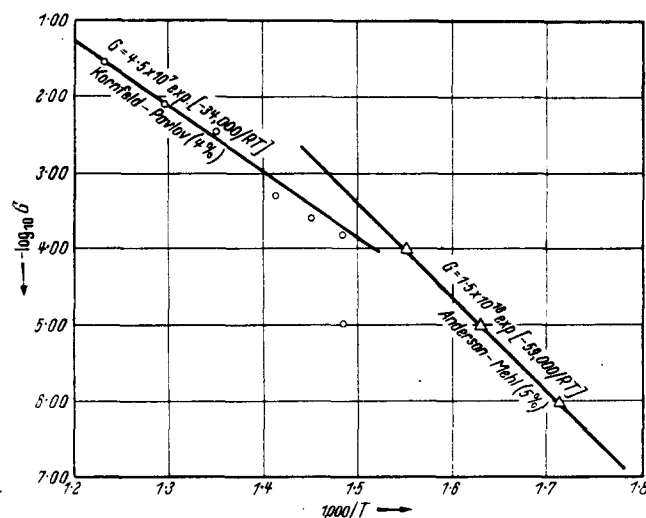


Figure 9. $\log G$ as a function of $1/T$ in the recrystallization of fine-grained aluminium

to draw a continuous curve (*Figure 9*) through the experimental point of both investigations so that the maximum deviations are little more than the experimental error.

In the recrystallization of heavily deformed rock salt crystals¹² two values of Q_G are required to describe the data (*Table II*)—one valid in the range 400 to 800°C and the lesser value valid in the low temperature range 300° to 400°C. This variation of $\log G$ with $1/T$ is similar to the variation of $\log S$ with $1/T$ where S is the specific conductivity of rock salt crystals. It is found that two activation energies are required to describe the results with the lesser valid in the low temperature range.

Included in *Table II* are activation energies $Q^{19, 27, 28}$ evaluated from the slope of straight lines obtained by plotting $\log (1/t_c)$ against $1/T$, where t_c is the time required for a constant fraction $X = c$ of the specimen to recrystallize. Q is not necessarily identical to Q_G because it is also partly determined by the activation energy for nucleation Q_N . However, for the cases considered Q proved to be independent of X within experimental error and the most reasonable interpretation of this fact is that $Q_N \approx Q_G \approx Q$.

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Table II

Substance	Primary Recrystallization		G_0 cm sec ⁻¹	Q kcal/gm atom
	Temperature Range °C	Strain % (reduction in area)		
Aluminium ¹³	425-540	4	4.5×10^7	34.0
Aluminium ²³	310-370	5.1	1.5×10^{18}	59.0
Rock salt ¹²	650-770	1,000* gm/mm ²	9×10^{11}	59.0
Rock salt ¹²	400-520	4,000* gm/mm ²	4.2×10^8	32.0
Rock salt ¹²	320-400	4,000* gm/mm ²	10^3	14.5
Copper ¹¹	300-360	10	10^{13} to 10^7	50.0 to 32.0
Copper (OFHC) ²⁷	200-250	99.7	†	29.9
Copper (spec. pure) ²⁷	40-140	98	†	22.4
Copper ¹³	25-125	99	†	44.0
Silicon ferrite ²⁴	740-800	7	1.7×10^{11}	73.0
Nickel-iron ²⁸	500-600	98	†	56.5
Secondary recrystallization				
Silver ²⁶	433-533		2×10^3	28.0
Copper (OFHC) ²⁵	900-1000†		10^{11}	73.0
Copper (spec. pure) ²⁹	500-520		10^{23}	95.0
	580-600		$10^{6.4}$	29.4
Grain Growth				
	Temperature Range	aG_0 cm sec ⁻¹	Q_G kcal/gm atom	
Aluminium ³⁶ (0.3 mm grain size)	400-500	10^{21}	87.0	
α -Brass (comm. purity) ³⁹	450-700	10^8 to 10^9	60.0	
α -Brass (high purity) ⁴⁰	450-850	0.83×10^4	40.0	

* Expressed as stress on specimen rather than strain.

† G_0 cannot be calculated from data.

‡ Both Q_G and G_0 decreased very sharply ($Q_G \rightarrow 0$) at temperatures approaching the melting point.

Strain (ϵ)—The available data on the relation between G and ϵ at constant temperature for metals ^{11, 13, 23, 24} show that G increases as ϵ^n , where n is substantially greater than unity, for small strains ($\epsilon < 5$ –10 per cent). For larger strains ($\epsilon > 15$ –20 per cent) the indications are⁴ that G is practically independent of strain. Anderson and Mehl's measurements²³ on G as a function of ϵ in the recrystallization of high purity aluminium at 329°C are plotted in Figure 10. Their results clearly show a sigmoidal relation between G and ϵ consistent with the above generalizations with G approaching a constant value at $\epsilon \approx 15$ per cent.

The limited data available^{12, 23} indicate that both Q_G and G_0 decrease with increasing strain. According to Anderson and Mehl Q_G for aluminium decreases from 62 kcal/gm atom at $\epsilon \approx 2$ per cent to about

52 kcal/gm atom at $\varepsilon \approx 20$ per cent, while G_0 decreases by a factor of approximately 10 over the same range of strain. Müller correlated G for rock salt with stress rather than strain.¹² His measured Q_G values are plotted against stress in Figure 11. They fall sharply from a value of approximately 60 kcal/gm atom at a stress to 10^5 gm/cm² to a limiting value of approximately 30 kcal/gm atom at stresses ranging from 2×10^5 to 4×10^5 gm/cm². G_0 decreases by a factor of about 200 as the stress increases from 10^5 to 2×10^5 gm/cm².

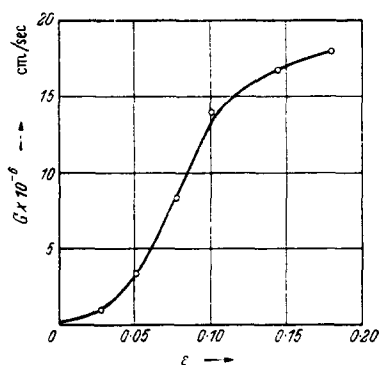


Figure 10. G as a function of strain, ε , in the recrystallization of aluminium

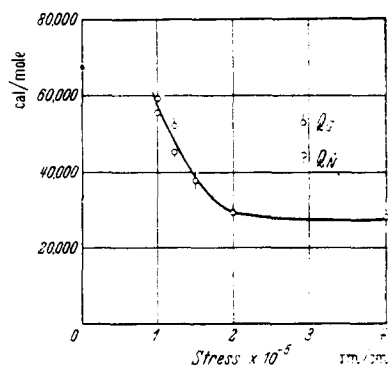


Figure 11. Activation energy for N and G as a function of stress in the recrystallization of rock salt single crystals

For both aluminium and rock salt the change in Q_G with increasing strain is of the order of 1,000 times the magnitude of the energy of cold deformation. However, G_0 tends to change with increasing ε in a way that partly compensates for the change in G due to the decrease in Q_G .

It has been proved by BECK and POLANYI⁴¹ that G is very dependent upon the specific type of deformation as well as upon the overall strain.

Aluminium single crystals were bent and approximately one half of each crystal was re-straightened. The re-straightened part of the crystal P_1 proved to be harder than the portion that remained bent P_2 yet G was very much larger in P_2 than in P_1 .

Recovery Anneal—The available data^{12, 13} indicate that recovery anneals (extended heat treatments at temperatures too low to cause visible recrystallization, but sufficiently high to alter the mechanical and electrical properties of cold worked materials) have no perceptible effect on G measured in subsequent recrystallization treatments. It should be noted, however, that these results do not rule out possible recovery effects on G at the recrystallization temperature during the nucleation period.

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Purity—It is well known to metallurgists that minute quantities (often < 0.01 per cent) of impurities may decrease the rate of recrystallization by many orders of magnitude so that the temperature of perceptible recrystallization is increased several hundred degrees. For example, SMART and SMITH⁴² have shown that the 'half softening' temperature, $T_{1/2}$ of spectroscopically pure (99.999 per cent) copper may be increased more than 200° by the addition of traces of certain solute impurities. No quantitative conclusions regarding the magnitude of \dot{N} and G can be drawn from the data, but they probably indicate the temperature range (centring around $T_{1/2}$) in which recrystallization takes place at an easily measured rate. The results for several solute elements (0.01 per cent by weight) are shown in *Table III*.

Table III. Data of Smart and Smith⁴² showing Effect of Impurity Traces on Softening Temperatures

Element in copper 0.01 per cent by weight	Half softening temperature $T_{1/2}$ ($^{\circ}\text{C}$)
None	140
Silver	205
Antimony	320
Cadmium	305
Tin	315
Tellurium	370

It appears that Müller has obtained the only quantitative data¹² on the effect of a controlled amount of a specific impurity on G . For deformed rock salt crystals containing 0.005 molecular per cent strontium chloride, $G \sim 1/12$ the value for similarly deformed crystals containing no added strontium chloride. Within experimental error, Q_G is independent of the amount of strontium chloride up to 0.005 molecular per cent. However, the interpretation of Müller's results is rendered ambiguous by the fact that G values for different compositions were compared at constant stress and it is not known whether or not the strain was constant.

An interesting effect obtained by Müller is that the periodic fluctuations in growth rate are imperceptible in rock salt crystals containing as little as 0.0025 molecular per cent of strontium chloride. On the other hand, in crystals containing 0.005 molecular per cent strontium chloride, G sometimes falls abruptly to zero before impingement.

Effects of Variables on \dot{N}

Time—It has been established that in the recrystallization of lightly deformed fine-grained specimens of aluminium and silicon ferrite

$\dot{N} \simeq 0$ at $t = 0$ and increases sharply with increasing time. Kornfeld and Pavlov first observed¹³ this effect in the recrystallization of aluminium wires of commercial purity and found that \dot{N} was best described by the equation

$$\dot{N} = kt \quad \dots (28)$$

For high purity aluminium and silicon ferrite strip Mehl and co-workers found²²⁻²⁴ \dot{N} to be given by equation 25 (see graphical relation in *Figure 12a*).

In the recrystallization of lightly deformed coarse-grained aluminium strips Anderson and Mehl found²³ that \dot{N} rises from zero to a maximum at τ_{\max} and then falls to zero asymptotically as shown in *Figure 12b*.

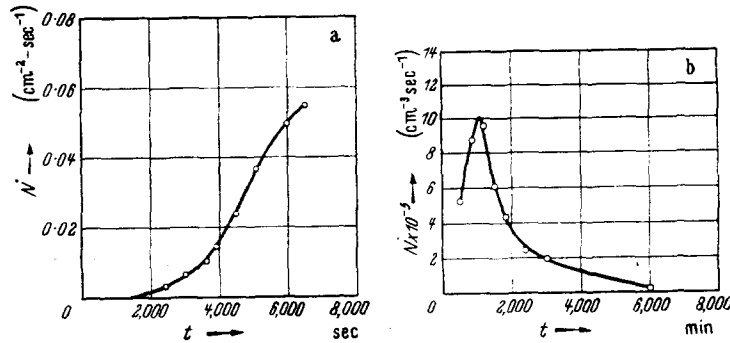


Figure 12. \dot{N} as a function of time in the recrystallization of a fine-grained and b coarse-grained (60 grains/mm²) aluminium; temperature = 350°C, $\varepsilon = 0.05$

Müller observed¹² that recrystallized grains always originate in the vicinity of the corners of deformed cubical rock salt single crystals. For a given load and temperature τ was, remarkably, reproducible to ± 3 per cent. This result can be interpreted on the basis that $\dot{N} (\propto 1/\tau)$ at the cube corner sites increases very sharply with time and much more so than in the recrystallization of polycrystalline aluminium. Only one nucleus forms per corner site because the amount of material available for nucleation is quickly consumed by crystal growth.

It has been observed also that \dot{N} increases sharply with time in the secondary recrystallization of cube texture copper,²⁵ following equation 25.

Thus, for conditions such that only a relatively small number of crystals form in either primary or secondary recrystallization, \dot{N} generally increases sharply with time and goes to zero at $\tau = 0$.

In the recrystallization of heavily deformed polycrystalline aggregates \dot{N} can be deduced from isothermal recrystallization data only with the aid of special assumptions and no generalization on the relation of

\dot{N} with τ for these conditions can be made. As already noted Decker and Harker interpret their data²⁷ on copper on the assumption that $\tau = 0$ for all grains but interpretations based on the concept that \dot{N} is independent of time can also account for their data. The possibility that \dot{N} increased with time in their experiments or those of Cook and RICHARDS¹⁹ is very remote.

Temperature—Since \dot{N} is generally a sensitive function of time the problem arises on how to compare \dot{N} at different temperatures. Several solutions have been proposed as follows:

- a* express the constants of the equation $\dot{N} = f(t)$ as functions of temperature (Kornfeld and Pavlov, and Anderson and Mehl)
- b* compare \dot{N} at various temperatures for $X = \text{constant}$ (Anderson and Mehl)
- c* compare \dot{N} at various temperatures for a constant number of grains nucleated (*i.e.* compare τ of the n th grain at various temperatures; method of Müller).

From the standpoint of a complete description of the process of recrystallization it is most desirable to adopt method *a* for expressing \dot{N} as a function of temperature. This procedure involves finding $k = f(T)$ for the Kornfeld-Pavlov equation, a and b as $f(T)$ for the Stanley-Mehl equation, and \bar{N} and $\nu = f(T)$ for the Avrami equation. When the just recrystallized grain size D_0 is independent of temperature methods *b* and *c* give identical results and \dot{N} for all times at a given strain and temperature is described by a single activation energy $Q_{\dot{N}}$ that is identical to the activation energy for grain growth Q_G . For this reason method *b* or *c* is the most useful way of expressing $\dot{N} = f(T)$ when D_0 is independent of T . However, when $D_0 = f(T)$ it appears that method *a* is the only meaningful way of describing $\dot{N} = f(T)$.

Generally it is found that $Q_{\dot{N}}$ evaluated by methods *b* and *c* is very nearly equal to Q_G in recrystallization. In *Figure 11* the Q_G and $Q_{\dot{N}}$ values measured by Müller on rock salt (high temperature range) are plotted against stress and it is evident that within the experimental uncertainty, they fall on identical curves. EASTWOOD *et al.*,⁴³ and WALKER⁴⁴ have demonstrated that D_0 for α -brass is independent of temperature thus indicating that $Q_{\dot{N}} = Q_G$ for all strains in the recrystallization of α -brass. Also in the recrystallization of silicon ferrite²⁴ $Q_G \simeq Q_{\dot{N}}$.

The results on aluminium²³ indicate that $Q_{\dot{N}} \simeq Q_G$ for tensile strains of the order of 10 per cent or greater. However, for very small elongations (of the order of 5 per cent or less) Anderson and Mehl found that $Q_{\dot{N}}$ measured by method *b* was significantly greater than Q_G . In general agreement with this result Kornfeld and Pavlov found that

$d \log_e k/dT$ ($k = \dot{N}/t$) at 4 per cent elongation was very much greater at all temperatures than $(d/n G/dT)$. However, k could not be described by a single activation energy. Generalizing, $Q_{\dot{N}} \approx Q_G$ excepting that for very small strains ≤ 5 per cent $Q_{\dot{N}} > Q_G$.

Strain (ϵ)—In the recrystallization of rock salt crystals it was observed that $1/\tau$ varies by the same factor with a change in stress as does G . If $1/\tau$ for the n th grain in the recrystallization of metals changed with strain by the same factor as G then D_0 would be independent of strain as well as temperature.

However, for metals D_0 generally decreases with increasing ϵ as indicated by the typical results for α -brass⁴³ as plotted in Figure 13.

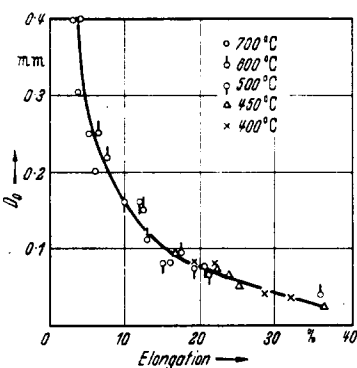


Figure 13. D_0 at several temperatures as a function of prior strain for α -brass

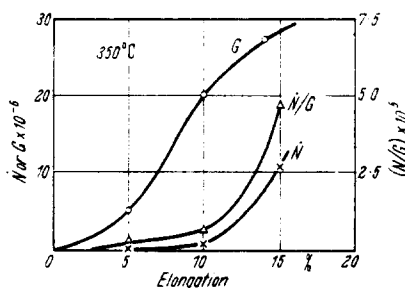


Figure 14. \dot{N} , G and \dot{N}/G as a function of strain in the recrystallization of aluminum

Since $Q_{\dot{N}} \approx Q_G$ for all strains this result requires that \dot{N} increase by a much larger factor with an increase in ϵ than does G (see equation 29).

In the recrystallization of lightly deformed aluminium the fact that $Q_{\dot{N}}$ is greater than Q_G at small strains is perhaps the most important factor in determining that D_0 becomes very large for small ϵ . In aluminium and silicon ferrite the approximate relation between \dot{N} and ϵ at constant T is^{23, 24}

$$\dot{N} = C \exp (k\epsilon) \quad \dots \quad (29)$$

In Figure 14 \dot{N} and G are plotted against ϵ for the three dimensional recrystallization of high purity aluminium. Apparently G becomes an insensitive function of ϵ where \dot{N} is still changing rapidly. D_0 is a function³ of the ratio \dot{N}/G (Figure 14) and increases rapidly with ϵ .

Prior Recovery Treatments—Kornfeld and Pavlov have shown¹³ that in polycrystalline aluminium of commercial purity \dot{N} is greatly decreased by a 20 hr recovery anneal at 320°C, though G is unaffected. Without the recovery anneal the mean τ was 8 min compared with 36 min for samples subjected to a recovery anneal. On the other hand,

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Anderson and Mehl found²³ no measurable effect of recovery anneals in the recrystallization of high purity aluminium strip.

Stanley found²⁴ that \dot{N} was decreased in polycrystalline silicon ferrite (7 per cent elongation) as a result of a recovery anneal. However, the observed effect is quite small and of borderline significance.

In natural single crystals of rock salt Müller found¹² that a 1 hr recovery anneal at 500°C increased τ at 590°C by a factor of 2.2.

Collins and Mathewson observed²¹ that \dot{N} in high purity aluminium single crystals is decreased markedly by recovery anneals. On the other hand, quite a different implication has been drawn from the following results of KORNFIELD and SCHAMARIN⁴⁵ on deformed aluminium single crystals of commercial purity:

- 1 the just recrystallized grain size is smaller in specimens subjected to a recovery anneal than in those not given this anneal
- 2 G is not changed by the recovery anneal.

These results prove that \dot{N} is increased by the recovery anneal for the time interval ($t_1 - t_2 = \Delta t$) at the recrystallization temperature during which grains appear. The usual interpretation assumes that t_1 has about the same magnitude whether or not the specimen has been subjected to a recovery anneal. However, an alternative interpretation that fits the facts as well and that has different theoretical implications is that t_1 for specimens given a prior recovery anneal is much larger than for specimens given no prior recovery treatment.* Since Kornfeld and Schamarin did measure G it seems likely that they noted t_1 , and found it not essentially changed due to recovery treatments. In any event the general result is in disagreement with that of Collins and Mathewson.

Summarizing, it is apparent that the general effect of prior recovery treatments on \dot{N} for either polycrystalline or single crystal specimens is far from clear at the present time.

Purity—Müller has observed that the addition of traces of (0.005 molecular per cent) strontium chloride to pure rock salt crystals decreases the reciprocal of the nucleation period $1/\tau$ and G by practically an identical factor (approximately 12). However, neither $Q_{\dot{N}}$ nor Q_G is changed by the impurity for a constant stress.

There seem to be no quantitative data available on the effect of impurities on \dot{N} in metal systems.

Distribution of Nuclei in Recrystallization—It is significant that recrystallized grains do not originate at random in a strained matrix but preferentially at intersecting slip lines, strain markings, twin

* In different words Kornfeld and Schamarin's reported facts do not eliminate the possibility that the mean nucleation period $\bar{\tau}$ is larger for 'recovered' specimens than for 'unrecovered' specimens.

boundaries and often at a free surface, edges or grain boundaries. *Figure 15* shows a small recrystallized grain formed in a cluster of slip lines.⁴⁶ These preferential nucleation sites are generally supposed to be regions in which the stress is much higher than in the surrounding matrix.

Grain Size—In general the larger the grain size the smaller is \dot{N} . In fine-grained aluminium or copper specimens \dot{N} is measurable for strains of 5 per cent or less. On the other hand for certain orientations of copper or aluminium crystals strained 20 to 30 per cent in tension \dot{N} is virtually zero. Anderson and Mehl's more quantitative data²³ on aluminium also shows that \dot{N} decreases markedly with increasing grain size.

Interpretation of the Effect of Variables on G

In the following sections we shall derive a general expression for G , compare the values computed from it with experimental ones, attempt to rationalize the apparent discrepancies between theory and experiment and finally offer some qualitative explanations of the effect of variables on grain boundary migration. So many variables can operate to influence the rate of boundary migration that the existing observations can be explained on the basis of many different hypotheses. There remains a need, however, for quantitative measurements that will permit decisions to be made on the validity of the various hypotheses.

Theory of Kinetics of Boundary Migration—With the aid of some simplifying assumptions we shall derive from rate theory a general expression for G that can serve as a 'handle' for the theoretical discussion of the problem. The formalism of the absolute reaction rate theory⁴⁷ will be followed. The method is entirely analogous to that used in deriving expressions for the rate of growth of crystals,^{48, 49} into supercooled melts and the final result is similar in form. Recently MOTT⁵⁰ has, in effect, applied the theory to crystal growth in recrystallization.

Consider the energy of transfer of an atom across an interface from one grain to another where the driving energy is either strain or surface energy. Schematically the free energy of the atom in its various configurations may be represented as in *Figure 16*. In this figure, A and B are represented as crystal sites on opposite sides of a grain boundary. Either because of strain or boundary curvature (see sections on grain growth and effect of variables on G) the free energy of an atom in site B is greater than in site A by an amount ΔF per gm atom. ΔF_A is the free energy difference per gram atom between an atom in the activated state and state B . Let the jump frequency in the direction of A - B interchange be $\nu = kT/h$ in conformity with absolute rate



Figure 15. A small grain growing in a highly strained region (magnification 2000 \times)

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theory. Then the frequency of jumping of an atom from a B to an A site f_{BA} is given by:

$$f_{BA} = (kT/h) \exp [-(\Delta F_A)/RT] \quad (30)$$

and the frequency of jumping from an A to a B site f_{AB} is:

$$f_{AB} = (kT/h) \exp [-(\Delta F_A + \Delta F)/RT] \quad (31)$$

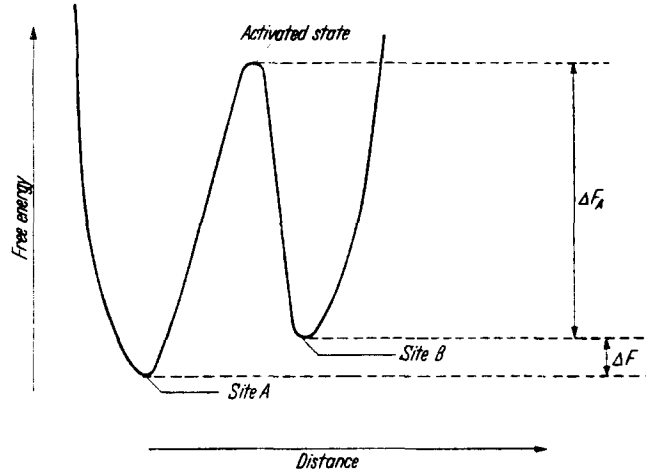


Figure 16. Schematic representation of free energy state of crystal sites on opposite sides of a grain boundary

The net rate of transfer per atom f is:

$$f = f_{BA} - f_{AB} = (kT/h) \exp [-(\Delta F_A)/RT] [1 - \exp (-\Delta F/RT)] \quad (32)$$

f is related to the linear rate of growth G by the equation:

$$f = G/\lambda \quad (33)$$

where λ is the interatomic spacing in the interface. Thus:

$$G = (kT/h)\lambda \exp [-(\Delta F_A)/RT] [1 - \exp (-\Delta F/RT)] \quad (34)$$

In recrystallization ΔF may be equated to \mathcal{Z} the mean strain free energy* per gram atom in the recrystallized metal where it is assumed that \mathcal{Z} is spread uniformly† throughout the strained matrix. When boundary migration is driven by surface energy

$$\Delta F = K\sigma V/r \quad (35)$$

* There are no data which relate \mathcal{Z} to the energy of cold working ΔH measured⁹ by Taylor and Quinney and in fact any such relation cannot be deduced with the methods of classical thermodynamics. In the following discussion it will be assumed without justification that $\mathcal{Z} = \Delta H$.

† For example it may be supposed that \mathcal{Z} is contained entirely in the surface energy σ of sub-boundaries formed in cold working. Then $\mathcal{Z} = K\sigma V/r$ where r is the linear dimension of the sub-boundary.

where r is the boundary radius of curvature, V is the gram atomic volume of the metal and K is a constant of the order of 1 to 3. In any event ΔF is generally very small in relation to RT , for the maximum value of ζ known to have been realized experimentally is of the order of 25 to 100 cal/gm atom⁹, while free energies due to surface energy are much smaller for realizable grain sizes. Consequently

$$1 - \exp [-\Delta F/RT] \simeq \Delta F/RT \quad (36)$$

ΔF_A can be expressed as follows:

$$\Delta F_A = Q_G - T\Delta S_A - RT \quad (37)$$

where Q_G is the measured activation energy and ΔS_A is defined as the difference in entropy between the atom in its activated state and in site B . Substitution of equations 36 and 37 into equation 34 gives in general:

$$G = e(kT/h)\lambda(\zeta/RT) \exp [\Delta S_A/R] \exp [-Q_G/RT] \quad (38)$$

in boundary migration due to strain energy, and

$$G = e(kT/h)\lambda(K\sigma V/rRT) \exp [\Delta S_A/R] \exp [-Q_G/RT] \quad (39)$$

in boundary migration due to surface energy. In equation 38 ΔS_A and Q_G can in general be orientation and strain dependent.* In equation 39 σ , ΔS_A and Q_G can be orientation dependent.

Comparison of Theoretical and Experimental Values of ΔF_A , Q_G and ΔS_A — It has been pointed out (p 234) that G could be represented by equation 27 where G_0 and Q are in general functions of strain and relative grain and boundary orientations. From equation 38:

$$G_0 = e(kT/h)\lambda(\zeta/RT) \exp [\Delta S_A/R] \quad (40)$$

for boundary migration due to strain and

$$G_0 = (kT/h)\lambda(K\sigma V/rRT) \exp [\Delta S_A/R] \quad (41)$$

for boundary migration due to surface energy.

Experimentally measured values of G_0 are shown in *Table III*. Reasonable estimates of all the quantities excepting ΔS_A entering into equations 40 and 41 can be made. For comparing theory with experiment there are the alternatives of either treating ΔS_A as a disposable parameter and drawing inferences about the activated state from its magnitude, or calculating G_0 absolutely on the assumption that ΔS_A is identical in value with ΔS_A in self-diffusion (preferably grain boundary self-diffusion).

* Note that although the difference in free energy of an atom in A and B sites is accounted for by ζ , the height of the activation hill and therefore, Q_G and ΔS_A can be strongly dependent upon strain.

ΔS_A and ΔF_A values calculated from measured G_0 values by assigning the following numbers to the quantities in equations 40 and 41: $e = 2.72$, $(kT/h) = 10^{13} \text{ sec}^{-1}$, $\lambda = 2 \times 10^{-8} \text{ cm}$, $(K\sigma V/rRT) = 10^{-4}$, $Z/RT = 10^{-2}$, are listed in *Table IV*. For comparison the entropies and free energies of activation calculated from diffusion data are also given. In calculating ΔS_A and ΔF_A from grain growth data it was assumed arbitrarily that $a = 1$ (*Table III*).

From the results of these calculations the generalization can be made that $(\Delta F_A)_G < (\Delta F_A)_L$ where $(\Delta F_A)_L$ is the free energy of activation for lattice self-diffusion (as distinguished from grain boundary self-diffusion). Mobility B is defined as velocity per unit potential gradient and for ideal solutions has the following relation to the diffusion coefficient D :

$$B = D/kT \quad (42)$$

If B_G be the mobility of atoms in grain growth and B_L the mobility of atoms in self-diffusion, it follows that:

$$B_G \propto \exp [-(\Delta F_A)_G/RT] \quad (43)$$

and

$$B_L \propto \exp [-(\Delta F_A)_L/RT] \quad (44)$$

From the relative magnitudes of $(\Delta F_A)_G$ and $(\Delta F_A)_L$ it follows that $B_G \gg B_L$ for all the measurements reported in *Table III*. This result is expected because of the supposed large degree of disorder at crystal interfaces. However, it should be noted that wrong inferences about the magnitude of B_G and B_L would have been made in many cases by equating B to $\exp [-Q/RT]$ as is often done.

It may be significant that for silver $(\Delta F_A)_G$ ($\approx 21.5 \text{ kcal/gm atom}$) is in much closer agreement with the free energy of activation for grain boundary diffusion $(\Delta F_A)_B$ ($\approx 18.6 \text{ kcal/gm atom}$) than with $(\Delta F_A)_L$ ($\approx 39.0 \text{ kcal/gm atom}$). Comparison of $(\Delta F_A)_B$ and $(\Delta F_A)_G$ for other substances would be very interesting, but cannot yet be made because of the lack of data on grain boundary self-diffusion. Certainly it is expected in general that $(\Delta F_A)_G$ should be closer in magnitude to $(\Delta F_A)_B$ than to $(\Delta F_A)_L$.

Although the relation between $(\Delta F_A)_G$ and $(\Delta F_A)_L$ is in qualitative accord with expectations based on theories of crystal interface structures the relations between the corresponding energies of activation (Q_G against Q_L) and entropies of activation [$(\Delta S_A)_G$ against $(\Delta S_A)_L$] are more difficult to explain. On the basis of the simple qualitative picture it might be expected that $Q_G < Q_L$ and that $(\Delta S_A)_G \ll (\Delta S_A)_L$. Actually, with few exceptions, $(\Delta S_A)_G$ is much larger than $(\Delta S_A)_L$ and Q_G is of the same order of magnitude or even somewhat larger than Q_L .

Rationalization of Discrepancies between Theory and Experiment—There are a number of ways in which the disagreement between the qualitative theoretical expectations on the correlation of $(\Delta S_A)_G$ to $(\Delta S_A)_L$ and of Q_G to Q_L and the experimental values can be explained. Mott has attempted⁵⁰ to rationalize the large value of $(\Delta S_A)_G$ by assuming that several atoms are activated in the unit process. Alternatively, it can be assumed that the measured values of Q_G are not representative of a single process, and are higher than the activation energy required for the transfer of a single atom across a boundary. As a consequence the computed value of $(\Delta S_A)_G$ is too high. Also large apparent values of Q_G might result from changes in the ΔF of equation 34 with temperature as a result of recovery or the solution of inclusions. Hypotheses that will explain these discrepancies are set forth in the following sections, but further quantitative experimental work is needed to show whether any of them can adequately explain the facts.

Mott Hypothesis—Mott has attempted⁵⁰ to resolve the problem of the apparently unreasonably large $(\Delta S_A)_G$ by postulating that n atoms are activated in the unit process. He proposes that the activation free energy is in effect the free energy of ‘melting’ the n atoms that after melting are free to recrystallize on one side of the boundary or the other. The disposable parameter n may be calculated from the experimental $(\Delta F_A)_G$ by the relation:

$$n(\Delta F) = (\Delta F_A)_G \quad (45)$$

where ΔF is the free energy increase on melting at temperature T . Approximating ΔF by the relation:

$$\Delta F = Q_f(1 - T/T_0)$$

where Q_f is the gram-atomic heat of fusion and T_0 the absolute melting temperature he obtains:

$$G = e(kT/h) (\lambda n \zeta / RT) \exp [nQ_f/RT_0] \exp [-nQ_f/RT]. \quad (46)^*$$

Mott’s theory reduces the number of disposable parameters from two [Q_G and $(\Delta S_A)_G$] to one (n) and may be tested by comparing $(\Delta S_A)_G$ with $nQ_f/T_0 = n\Delta S_f$. Here ΔS_f = entropy of fusion per gram atom and n is calculated from the relation:

$$nQ_f = Q_G \quad (47)$$

The comparison between $n\Delta S_f$ and $(\Delta S_A)_G$ is shown in *Table IV*.

Although the agreement is good in some instances (*e.g.* Anderson and Mehl’s aluminium data,²³ Ward’s data on copper²⁵) in almost as many cases the agreement of $(\Delta S_A)_G$ with $(\Delta S_A)_L$ is equally good.

* We have modified Mott’s equation slightly setting $v = kT/h$ and introducing the factor e in order to conform to the formalism of the absolute reaction rate theory.

Table IV

Substance	Strain % R.A.	Temp. range °C	ΔS_A cal/deg gm atom				Q kcal/gm atom			$\Delta F_A $		
			$(\Delta S_A)_B$	$(\Delta S_A)_L$	$(\Delta S_A)_G$	$n\Delta S_f$	Q_B	Q_L	Q_G	$(\Delta F_A)_B$	$(\Delta F_A)_L$	$(\Delta F_A)_G$
			Primary Recrystallization									
Aluminium ¹³	4	425-540		9.2*	18	36		37.5†	34.0		30.5	20.0
Aluminium ²³	5.1	310-370			58	63			59.0		32.0	24.5
Rock salt ¹²	1,000 gm/mm ²	650-770		18.4	39	55		51.4‡	59.0		33.0	20.0
	4,000 gm/mm ²	400-520			23	30			32.0		38.0	15.0
Copper ¹¹	10	300-320		14.0	43	37		57.2 ⁵²	50.0		49.0	24.0
	10	340-360			15	24			32.0		48.8	22.5
Silicon ferrite ²⁴ ..	7	740-800		13.0	35	41		59.7§	73.0		46.2	36.5
			Secondary Recrystallization									
Copper ²⁵		900-1000		14.0	43.0	54.0		57.2	73.0		40.4	21.5
Silver ²⁶		433-533	2	9	7.4	23	20.2 ¹¹⁰	46.0 ⁵¹	28.0	18.6	39.0	21.5
			Grain Growth									
Aluminium ³⁸ ..	0.03 cm grain size	400-500		9.2	88	93		37.5	87.0		31.0	23.3
α -Brass (com. purity) ³⁹		450-700			31.0				60.0			33.6
α -Brass (high purity) ⁴⁰		450-800			10.0				40.0			31.0

* Estimated from DUSHMAN-LANGMUIR equation. † Calculated from correlation of Q_L with heat of sublimation.⁵² ‡ From anion conductivity data.⁵³

§ From self-diffusion in α -iron⁵⁴

|| The average value of T was used to compute ΔF_A from eq. 37

There are several plausible alternative hypotheses for the abnormal magnitude of $(\Delta S_A)_G$ that merit consideration.

Recovery Hypothesis—In supposing that the rate of boundary migration is controlled by a single activation energy which is measurable from the slope of a $\log G$ versus $1/T$ straight line relation the tacit assumption is made that the driving free energy ΔF is essentially independent of time and temperature. The experimental evidence that G is independent of time supports the assumption that the strain energy \mathcal{Z} driving boundary migration in primary recrystallization is time independent during the period of observable boundary migration. However, the possibility remains that \mathcal{Z} is reduced by recovery processes which essentially go to completion prior to the detection of recrystallized grains. If the degree of recovery thus is a function of temperature then the problem can be described by setting $\mathcal{Z} = f(T)$ where \mathcal{Z} is now the residual strain energy after the recovery process has run its course. G is independent of lower temperature recovery anneals because \mathcal{Z} at a given temperature is determined before new grains appear.

If \mathcal{Z} decreases with increasing temperature, as seems possible, the value of Q_G would apparently decrease for the same temperature variation. It was noted that Karnop and Sachs observed¹¹ that Q_G apparently decreased with increasing temperature and a similar conclusion for aluminium can be reached by combining KORNFIELD and PAVLOV's¹³ and ANDERSON and MEHL's²³ data. However, although the possibility of recovery must be taken into account in any theory of boundary migration, the recovery hypothesis alone provides no explanation for the fact that $(\Delta S_A)_G$ and Q_G are usually much larger than expected on the basis of rate theory and diffusion data.

In secondary recrystallization processes it is possible that $\sigma = f(t, T)$ and $r = f(t, T)$ (equation 39) due to concurrent grain growth in the matrix. However, since G values for these processes are also generally independent of time the equations must at least reduce to $\sigma = f(T)$ and $r = f(T)$. Thus $K\sigma V/r = f(T)$ and the description of the process becomes analogous to the description of primary recrystallization with $\mathcal{Z} = f(T)$.

Inclusion Hypothesis—It will be shown later that in the presence of inclusions the free energy decrease in boundary migration is given by

$$\Delta F' = K\sigma[1/r - \rho/r_0]V \quad (48)$$

where r_0 is the radius of the inclusion and ρ its volume fraction in the matrix. Equation 48 may be written

$$\Delta F' = \Delta F - M \quad (49)$$

where ΔF refers to strain or surface energy and M is an energy term due to inclusions and their dispersion. To take into account the

RECRYSTALLIZATION AND GRAIN GROWTH

effect of inclusions on the rate of boundary motion $\Delta F'$ must be substituted for ΔF in equation 34. If the number and size of inclusions retarding grain growth is unaffected by temperature, the measured value of Q_G will be identical to that measured on a specimen for which $M = 0$. However, if M is wrongly assumed to be zero the calculated $(\Delta S_A)_G$ will be smaller than it actually is. In general the number and volume of growth retarding inclusions will decrease with increasing temperature so that M will decrease as T increases. This

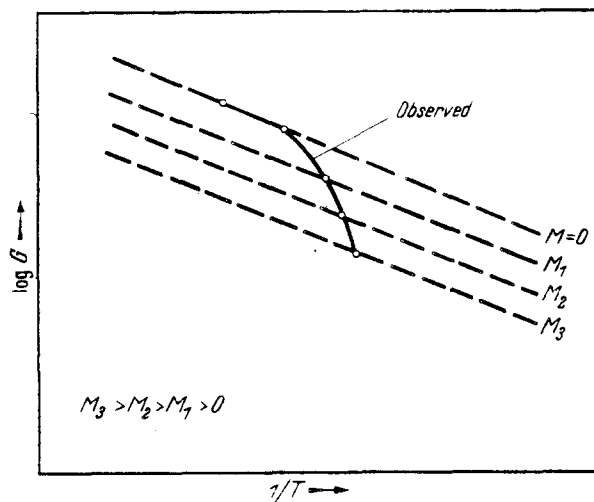


Figure 17. Schematic representation of $\log G$ as a function of $1/T$ for various degrees of dispersion, M , of inclusions at grain boundaries

variation of M with temperature will have the effect of making the apparent values of Q_G and $(\Delta S_A)_G$ larger than the values that would be measured with $M = 0$. In Figure 17 $\log G$ is plotted against $1/T$ for several supposed values of M . The curves are all parallel (*i.e.* Q_G is independent of M) but have different intercepts on the $\log G$ axis giving different apparent values of $(\Delta S_A)_G$. Now if M were fixed with temperature, one of the family of parallel curves would be deduced from a set of experiments. However, since $M = f(T)$ values of G measured at different temperatures will lie on a different curve of the family and the perceived temperatures of G will correspond to the hypothetical points shown in the diagram; thus apparent values of Q_G and $(\Delta S_A)_G$ will be calculated that are much greater than any set corresponding to a constant M .

In agreement with the theory just explained, Burke found⁴⁰ that Q_G for grain growth in high purity α -brass is 40 kcal/gm atom as compared with 60 kcal/gm atom for α -brass of commercial purity.

He also observed that the rate of grain growth in commercial purity brass could be increased many times by coalescing the inclusions and thus rendering them less effective. Also the inclusion hypothesis satisfactorily accounts for the variation of Q_G and $(\Delta S_A)_G$ with temperature observed by Ward, and Treafis and Turnbull in the secondary recrystallization of copper.

Inclusions can be effective in retarding boundary migration in primary recrystallization as well as in grain growth processes. In primary recrystallization retarded by inclusions equation 49 becomes:

$$\Delta F' = \mathcal{Z} - M \quad (50)$$

There is some evidence that inclusions do retard boundary migration in primary recrystallization. For example, the jerky motion of the boundary in the recrystallization of rock salt can be explained on the assumption that the slow motion occurs when inclusions lie in the moving boundary while the rapid motion occurs when the boundary moves. Whether or not the inclusion hypothesis applies to the rock salt results, it is clear that the average rate of motion of the boundary may not be the significant datum for comparison with the theory of boundary motion. Therefore, the values of Q_G and $(\Delta S_A)_G$ calculated by Müller to fit his data may be only apparent. Decker and Harker have found²⁷ that the activation energy for recrystallization of spectroscopically pure copper is about 7 kcal/gm atom less than that for recrystallization of OFHC copper. However, it is not certain whether this difference should be attributed to inclusions, soluble impurities or other factors.

If the driving energy for recrystallization \mathcal{Z} is directly proportional to the strain (as might be supposed for small strains from the data⁹ of Taylor and co-workers) then inclusions should be effective in retarding boundary migration only when the strain is the smallest necessary to produce recrystallization. As a consequence it is expected that in comparable temperature ranges Q_G should decrease sharply with increasing strains. In support of the inclusion hypothesis, Q_G is found to decrease sharply with increasing strain in the recrystallization of rock salt. However, in the recrystallization of aluminium Anderson and Mehl found²³ that Q_G is practically independent of strain between 2 and 8 per cent elongation in identical temperature ranges. Thus the inclusion hypothesis cannot be invoked to explain the very large value of $(\Delta S_A)_G$ calculated from Anderson and Mehl's results if it is supposed that \mathcal{Z} is proportional to the strain. On the other hand if because of recovery processes, the value of \mathcal{Z} effective in producing boundary migration is practically independent of strain ϵ the results of Anderson and Mehl for $\epsilon > 2$ per cent can be interpreted satisfactorily on the basis of the inclusion hypothesis.

Dependence of G on Strain—The factors of equation 40 derived from rate theory that might be dependent upon strain ϵ , are \mathcal{Z} , $(\Delta S_A)_G$ and Q_G . The simple hypothesis that $\mathcal{Z} \propto \epsilon$ and that Q_G and $(\Delta S_A)_G$ or more simply $(\Delta F_A)_G$ are independent of ϵ can be dismissed immediately on the basis of results for recrystallization after small strains. For example Anderson and Mehl observe that at 350°C G increases by a factor of about 20 for an increase in strain by a factor of 4. This change in rate with strain corresponds to a reduction in the free energy of activation for recrystallization of about 1.8 kcal/gm atom (compared to ≈ 21 kcal/gm atom total). Similar large decreases in $(\Delta F_A)_G$ at small strains with increasing strain have been observed by Müller, and Kornfeld and Pavlov, and are indicated by the result of Karnop and Sachs. On the other hand Anderson and Mehl found that G increases only slightly with ϵ for values of the latter ranging between 10 and 90 per cent reduction in area. This result is easily explained on the basis of the concept that recovery greatly reduces \mathcal{Z} at large strains and that $(\Delta S_A)_G$ and Q_G are independent of ϵ when it exceeds a critical amount. A hypothesis which may account for the extraordinary sensitivity of G to ϵ for ϵ very small ($\epsilon < 10$ per cent for aluminium) is that small strains increase by a large factor the number of lattice imperfections potentially capable of promoting boundary migration. Since the concentration of lattice imperfections \mathcal{V} is very small for a lattice in thermal equilibrium*, increasing \mathcal{V} by a factor of 10 for example would have no perceptible effect on the free energy of the lattice or on \mathcal{Z} . On the other hand such an increase in \mathcal{V} would increase the rate of lattice diffusion by a factor of 10 according to current theories. However, it is not clear how an increase in the concentration of imperfections that promote lattice diffusion will affect mobility of atoms at migrating boundaries.

Dependence of G on Orientations—When boundaries migrate, atoms at the boundary must occasionally move past other atoms as in diffusion. Qualitatively as Beck has suggested³⁵, one would expect the energy barrier for movement to be high where the mismatch between the grains is slight because the structure will be nearly continuous across the boundary and there will be little space for the atoms to move past each other. When the mismatch is greater, the structure should be more open, Q_G should be lower, and the rate of boundary migration higher.

Evidence has already been presented to show that the boundaries between grains which are of nearly the same orientation, or are nearly twinned orientations, migrate very much more slowly than boundaries where the disregistry is greater. On the other hand, polygonization

* It has been estimated that the concentration of lattice vacancies in thermal equilibrium with copper at 700°C $\approx 10^{-7}$.

boundaries apparently migrate readily, and at least many deformation twin boundaries migrate with similar ease. The usual mechanisms proposed for the migration of twin boundaries and for the movements of dislocations will permit the atoms to move in a manner necessary for the grain boundaries to migrate without requiring a loose packing of the atoms. When the special conditions necessary for the operation of these mechanisms exist, the boundaries will migrate readily even though the disregistry at the boundary is slight.

If the boundaries between grains of similar orientation do migrate slowly because the activation energy for the atom movements involved is larger, the rate of migration of these boundaries should increase more rapidly with temperature than the rate of migration of boundaries with lower activation energies. There are no measurements available of the activation energy for grain boundary migration as a function of the relative orientation of the grains, but there are numerous examples of the fact that a grain embedded in uniform matrix will grow more readily in certain directions than in others. This, undoubtedly, results from the fact that the position of the boundary controls its structure and hence its ability to migrate. COOK and RICHARDS⁵⁵ have observed anisotropy in the growth of new grains about an indentation in cube texture copper, and BOWLES and BOAS⁵⁶ have suggested that the 'rate of migration of a boundary in any direction is influenced by the change in orientation which occurs on crossing the boundary in that direction'.

The observations of KORNFIELD and RYBALKO³² and BURKE and TURKALO³³ that growth anisotropy is decreased with increasing temperature indicates that Q_G is greater for directions of rapid growth than for direction of slow growth.

Theory of Recrystallization Nuclei

Some of the principal facts that theories of recrystallization nuclei should explain are:

- 1 nuclei form preferentially in parts of the specimen where it appears that the degree of deformation is the highest
- 2 for small deformation \dot{N} increases with time
- 3 with few exceptions the activation energy for nucleation is not perceptibly different from the activation energy for boundary migration
- 4 \dot{N} increases sharply with increasing strain
- 5 generally there is a fairly well defined orientation relationship between the deformed matrix and the recrystallized grains.

Two general types of theories for recrystallization nuclei will be considered. One theory, that will be called the 'conventional nucleation

theory', supposes nuclei to grow in a highly strained part of the matrix by a sequence of thermal fluctuations from original dimensions approaching those of the atom. A second type of theory supposes that the nuclei are small 'blocks' or crystallites of the cold-worked matrix and the nucleation period, τ , results from an initial slow growth rate of the blocks. The slow growth rate is ascribed to various causes that will be considered in the following discussion.

Conventional Nucleation Theory

Consider an ordinary phase transformation

$$\alpha \rightarrow \beta$$

where α and β are in equilibrium at T_0 and β is the more stable phase when $T < T_0$. When α is cooled to $T < T_0$ there may be a nucleation period τ before β apparently starts to form. According to nucleation theory the free energy of small masses of β (called 'embryos') relative to α may be expressed as the sum of a free energy term proportional to the surface area of the mass and a free energy term proportional to its volume. Thus:

$$\Delta F = Ai^{2/3} + Bi \quad (51)$$

where i is the number of atoms in the β embryo, A is proportional to the interfacial free energy between α and β and B is proportional to the free energy released per unit volume when an infinite mass of α transforms to an infinite mass of β . At a given temperature when $B < 0$ ΔF goes through a maximum having coordinates:

$$\Delta F^* = (4/27) (A^3/B^2) \quad (52)$$

$$i^* = - (2A/3B)^3 \quad (53)$$

All embryos of β containing a number of atoms $i < i^*$ will tend to disappear while all aggregates containing a number $i > i^*$ will tend to grow and consume the α . According to the conventional theory the nucleation period τ is the mean time required at a given temperature for a sequence of fluctuations in the α matrix leading to the formation of a β 'nucleus' having the critical number of atoms i^* . The probability of such a sequence of fluctuations has been calculated for various kinds of phase transformations⁴⁸ and is proportional to $\exp [-\Delta F^*/kT]$. TURNBULL and FISHER⁵⁷ have shown that the rate of steady state (*i.e.* time independent) nucleation of crystals in a condensed system (mother phase liquid or solid) can be approximated by:

$$\dot{N} = n(kT/h) \exp [-(\Delta F_A)_G/RT] \exp [-\Delta F^*/kT] \quad (54)$$

where n is the number of atoms of the mother phase per unit volume.

To apply the theory to recrystallization, it is assumed that the cold-worked matrix is analogous to a metastable phase α which transforms

to a strain-free phase β . The driving energy for the transformation is the strain energy Z per cubic centimetre and the surface energy is the boundary energy between the strained and unstrained grains σ .

Assuming that the nucleus is a sphere of radius r^* it follows from equations 52 and 53 that:

$$\Delta F^* = (16\pi/3)\sigma^3/Z^2 = K\sigma^3/Z^2 \quad (55)$$

$$r^* = 2\sigma/Z \quad (56)$$

For recrystallization equation 54 may be rewritten as:

$$\dot{N}_\epsilon = n(kT/h) \exp [-(\Delta F_A)_G/RT] \exp [-K(\sigma_\epsilon)^3/(Z_\epsilon)^2 kT] \quad (57)$$

where \dot{N}_ϵ is the nucleation frequency in a region of strain ϵ . The plausibility of conventional nucleation theory can be tested by calculating \dot{N}_ϵ from equation 57 with reasonable assumed values of σ_ϵ and Z_ϵ .

Consider the formation of 'unstrained' embryos in a homogeneously sheared portion of a cubical lattice shown in *Figure 18*. Z_ϵ is given by the equation:

$$Z_\epsilon = (1/2) E\epsilon^2 \quad (58)$$

where ϵ is the shear strain and E is the shear modulus. It is clear from the figure that the embryo has a surface energy due to the elastic distortion at its boundary which exceeds the decrease in volume shear energy occasioned by its formation. A crude estimate of the surface energy can be obtained by assuming that the interface between large unstrained crystals and the strained lattice is made up of dislocations. The density of dislocations per unit length of boundary δ is approximately equal to the density δ' at a grain boundary B between two unstrained grains having an angle of misfit $\theta = \arctan \epsilon$. On this basis it is assumed that $\sigma_\epsilon = \sigma$ where σ is the surface energy of B . DUNN and co-workers^{37, 58} and CHALMERS and co-workers⁵⁹ have measured σ/σ_m where σ_m is the maximum grain boundary energy in the particular system, as a function of θ for a number of metals. From these data σ_ϵ can be calculated when σ_m is known.

The interfacial energy of high energy grain boundaries has been measured absolutely.^{10, 60, 61} FISHER and DUNN⁶² have surveyed the data critically and suggest 535 ± 50 erg/cm² as the best value of the Cu-Cu interfacial energy σ_{Cu} . By assuming further that $\sigma_{Cu} = \sigma_m$ and that the relation between σ/σ_m and θ for copper is identical with that found by Chalmers for lead grains rotated about a common [100] axis⁵⁹ numerical values can be assigned to σ_ϵ of copper embryos for given values of ϵ .*

* It is also supposed that σ_ϵ for nuclei is identical to σ_ϵ for large crystals. The validity of this supposition has been discussed elsewhere.³⁹

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Numerical values of r^* and \dot{N}_ϵ as a function of ϵ have been calculated for copper and are tabulated in *Table V*.

The observed nucleation frequency \dot{N} is related to \dot{N}_ϵ by the equation:

$$\dot{N} = \sum \dot{N}_\epsilon v_\epsilon \quad (59)$$

where v_ϵ is the volume fraction of material having strain ϵ . The results of the calculations indicate (*Table V*) that the only practically perceptible contribution to \dot{N} is made by regions where $\epsilon \geq 0.20$. For example, if $v_\epsilon = 10^{-6}$ for $\epsilon = 0.20$, $\dot{N} \geq 3.6 \text{ hr}^{-1} \text{ cm}^{-3}$. In regions where $\epsilon \approx 0.20$, $\mathcal{Z} \approx 350 \text{ cal/cm}^3$ but the total strain energy contained in all such regions (approximately 0.0004 cal/cm^3 for $v_\epsilon = 10^{-6}$) is

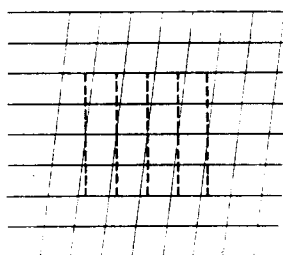


Figure 18. Unstrained embryo (---) in homogeneously sheared (—) square lattice

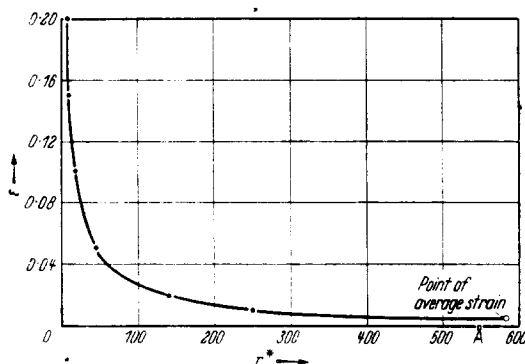


Figure 19. Critical radius for growth as a function of strain calculated on the basis of the model indicated in Figure 18

a negligible fraction of the average \mathcal{Z} (approximately 0.5 cal/cm^3) of the cold-worked specimen. Suppose that the average strain energy $\mathcal{Z} \approx 1 \times 10^7 \text{ erg/cm}^3$ corresponding to $\bar{\epsilon} \approx 0.005$. The theory of nucleation indicates that \dot{N}_ϵ in regions where $\mathcal{Z}_\epsilon = \mathcal{Z}$ is virtually zero. However, in order to grow at the expense of such regions, that constitute the major part of any specimen, a crystal must have attained the size $r > (r^*)_\epsilon$. Thus in the local region of very high strain where the nucleus forms, the distribution of strain must be such that $r > (r^*)$ for all values of the crystal size r after it has become a nucleus.

Figure 19 shows the relation between ϵ and r^* . The hypothesis that $\epsilon \approx 0.2$ in small regions of cold-worked metals does not seem to be inconsistent with any known experimental facts.

*Some Predictions of Conventional Theory Compared with Experience—*Conventional nucleation theory requires that the orientation relation between new crystals and the cold-worked matrix be such that σ_ϵ is a

minimum.* This condition leads in general to the fairly definite relation that the orientation of the nucleus be as nearly identical with the cold-worked matrix surrounding it as permitted by the elastic strains. The orientation relation for the example considered in the preceding section is clear from *Figure 18*. The prediction is consistent with the available experimental data since they do not eliminate the possibility that minor components of the recrystallization texture are always present in the cold-worked matrix.

The theory satisfactorily accounts for the existence of a nucleation period τ . The increase in \dot{N} with time follows directly from the theory⁶³ for immediately after quenching from the cold-worked state to the annealing temperature, the concentration of embryos of all sizes will be virtually zero and a considerable time will be required for the steady state distribution of embryos and nuclei assumed in deriving equation 54 to be established.

In agreement with experience, the theory predicts that nuclei will form preferentially in the most highly deformed parts of a cold-worked specimen. Also \dot{N} increases with decreasing grain size at a given strain because the volume v_s of regions that are highly stressed after deformation presumably increases with decreasing grain size.

If recovery anneals have the effect of decreasing v_s , then \dot{N} should, according to the theory, decrease due to such anneals. There is an alternative but less plausible possibility that nuclei form during the recovery period with the result that \dot{N} observed at the recrystallization temperature is greater than in the absence of a recovery treatment.

If σ_s , Z_s and v_s are essentially independent of temperature it follows from equations 57 and 58 that

$$Q_N \simeq Q_G + NK(\sigma_s)^3/(Z_s)^2 \quad \dots (60)$$

where N is Avogadro's number. From the results summarized in *Table V* it can be verified that $NK(\sigma_s)^3/(Z_s)^2$ is of the same order of magnitude as Q for $\epsilon \sim 0.2$ to 0.3 .

In the recrystallization of aluminium at small strains^{13, 23} Q_N is considerably greater than Q_G in agreement with theory but at moderate and large strains $Q_N \simeq Q_G$ for most substances in disagreement with theory. The disagreement can be resolved within the framework of the theory if either of the following assumptions is valid.

- 1 Measured values of Q_G are complex and larger than the activation energy for the elementary growth process for reasons discussed in the preceding section.

* It has been asserted that conventional nucleation theory predicts no preferred orientation relation between recrystallized grains and the matrix. Such assertions appear to have been based on the erroneous concept that a completely amorphous region of the cold-worked matrix is required for the operation of the conventional mechanism.

σ_e and Z_e are essentially temperature independent but v^* decreases sharply with increasing temperature due to a recovery process.

If $v_e \propto \exp [Q_R/RT]$ then as a gross approximation we have:

$$Q_{\dot{N}} = Q_G + NK(\sigma_e)^3/(Z_e)^2 - Q_R \quad (61)$$

Evidently for a singular range of E values $Q_{\dot{N}} \simeq Q_G$.

The data of Anderson and Mehl indicate²³ that the functional relations between $(Q_G - \epsilon)$ and $(Q_{\dot{N}} - \epsilon)$ are quite different for pure aluminium so that either of the above assumptions provides a credible rationalization of the relation of $Q_{\dot{N}}$ and Q_G for aluminium in terms of conventional theory. However, Müller found¹² that the relation $Q_G \simeq Q_{\dot{N}}$ holds quite closely for wide variations in applied stress (excepting at small stresses—*Figure 11*) and for significant changes in specimen purity in the recrystallization of rock salt single crystals. These results apparently are not compatible with the theory unless the implausible hypothesis is adopted that Q_R varies in the very singular way necessary to account for them.

Block Hypotheses

We shall now consider whether or not there are alternative mechanisms that permit nuclei to form more rapidly than they can form by the conventional nucleation mechanism. Several nucleation theories suppose⁵ that nuclei form from blocks (small crystallites) already existing in the cold-worked matrix by mechanisms whereby the block functions more or less as a unit. These blocks are sometimes considered to be crystallites that have received much less than the average deformation of the specimen ('low energy block hypothesis'). Other theories assume that they are crystallites that have received a much greater deformation than the crystal as a whole ('high energy block hypothesis'). These high energy blocks then become recrystallization nuclei, not by the mechanism outlined in the previous section, but by a sequence of unit processes that progressively relieve the strain in the *block as a whole*. For example if the block is strained by virtue of a high concentration of dislocations in its immediate vicinity, nucleation occurs by the migration of these dislocations elsewhere or by their mutual cancellation.

According to the block hypotheses, the nucleation period is a period of relatively slow growth of the block to macroscopic dimensions or it can be a period associated with the relief of strain energy within the block.

The general kinetics of block growth can be treated as a problem of time dependent grain growth. Equation 38 can be rewritten as:

$$G = dD/dt = k(\Delta F) \quad (62)$$

PROGRESS IN METAL PHYSICS

Table V. \dot{N} and r^* at Various Values of ε

ε	σ_e	$Z_e(\text{erg/cm}^3)$	$r^*(\text{\AA})$	$\dot{N}_e \text{ sec}^{-1} \text{ cm}^{-3}$
0.01	48	0.38×10^8	250	—
0.02	107	1.52×10^8	140	—
0.05	210	9.5×10^8	44	10^{-500}
0.10	310	38.0×10^8	16	10^{-100}
0.15	385	86.0×10^8	9	10^{-21}
0.20	450	152.0×10^8	6	10^3
0.30	500	342.0×10^8	3	10^{21}

$E = 7.5 \times 10^{11} \text{ erg/cm}^3$, $\sigma_m = 535 \text{ erg/cm}^2$, $(\Delta F_A)_\theta = 24 \text{ kcal/gm atom}$ (see Table IV),
 $T = 800^\circ\text{K}$

where D is the block size and

$$k = (\varepsilon \lambda \nu / RT) \exp [\Delta S / R] \exp [-Q_G / RT]$$

For D very large experience indicates that dD/dt is constant and the interpretation is that:

$$dD/dt \simeq k(\Delta F_0) \quad (63)$$

where ΔF_0 is independent of t as assumed in deriving equation 38. However, when the block is very small ΔF is a function of time and dD/dt may be expressed as follows:

$$dD/dt = k[\Delta F_0 - \Delta F(t)] \quad (64)$$

where $\Delta F(t)$ is a function that decreases with increasing time so that at very long times $\Delta F_0 \gg \Delta F(t)$. Integration of equation 64 gives:

$$D = k\Delta F_0 t - \int_0^t k\Delta F(t) dt \quad (65)$$

Comparison of equations 1 and 65 gives in general for $t > \tau$

$$\tau = (1/\Delta F_0) \int_0^t \Delta F(t) dt \quad (66)$$

In the sections that follow various types of block hypotheses will be considered in greater detail and τ calculated when possible.

Low Energy Block Hypothesis—Most theories on the origin of nuclei from low energy blocks are not explicit on the form of $\Delta F(t)$ or why the blocks have escaped deformation. One concept that leads to a definite form of $\Delta F(t)$ is that growth of the blocks is retarded by their surface tension. This concept is no different from the basic concept in conventional nucleation theory excepting that it is now supposed that

the initial block size $D_0 > 2r^*$. Expressing equation 51 in terms of D and ΔF per gram atom, we have

$$\Delta F = (-a\sigma D^2 + \zeta D^3)/D^3 = (\zeta - a\sigma/D) \quad (67)^*$$

where a is a geometrical factor and $\zeta > a\sigma/D$ for values of $D > D_0$. Substituting equation 67 into equation 62 and integrating, we have for D very large:

$$D = k\zeta \{t - (a\sigma/k\zeta^2) \ln [\zeta D/(\zeta D_0 - a\sigma)]\} \quad (68)$$

and by comparing equation 68 with equation 1, it follows:

$$\begin{aligned} \tau &= (a\sigma/k\zeta^2) \ln [\zeta D/(\zeta D_0 - a\sigma)] \quad (69) \\ &\simeq - (a\sigma/k\zeta^2) \ln [(\zeta D_0 - a\sigma)/\sigma] \end{aligned}$$

One possible source of low energy blocks for recrystallization nuclei is metal supposedly contained in cavities of small plastically undeformed

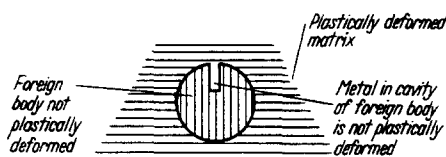


Figure 20. Unstrained part of metal retained in the cavity of a hard inclusion

inclusions that may be present in the cold-worked specimen. For example, consider a hard spherical foreign body (Figure 20), embedded in the matrix that contains a cylindrical cavity, filled with the matrix metal. The stress that deforms the matrix plastically is supposed to be not high enough to cause plastic deformation of the foreign body. The metal in the cavity does not plastically deform to an appreciable extent and may then serve as the low energy block in recrystallization.

It has been objected that the low energy block theory does not account for the preference of new grains for the sites of highest matrix deformation and for the fact that \dot{N} increases with ϵ . This objection is invalidated if the reasonable supposition is made that the low energy blocks are incapable of growth unless immediately surrounded by regions of very high strain energy. If this supposition is correct, the blocks must nucleate near sites of highest deformation and \dot{N} must increase with ϵ in agreement with experience. In the example considered (Figure 20) the low energy block cannot grow out of the cavity unless the strain energy released by its growth is greater than the increase in surface energy occasioned by its growth.

* In the sense that we are using ΔF and ζ , the surface energy term of equation 51 should be negative and the strain energy term positive.

In general, it is expected that the low energy blocks will have orientations closely approximating the orientation of the parts of the cold-worked matrix immediately surrounding them. This orientation relation will also obtain for nuclei originating from blocks retained in hard spherical inclusions. If σ , Z , and v_s are independent of temperature, the theory requires that $Q_N = Q_G$ in good agreement with most of the experimental data but in disagreement with the data on aluminium at small strains. The theory provides no clear explanation of the increase of \dot{N} with time at small ε .

High Energy Block Theories—High energy block theories suppose that at $t = 0$ $\Delta F(t) > \Delta F_0$ and consequently $dD/dt < 0$. In contrast to the mechanism for the decrease of $\Delta F(t)$ with time outlined under the conventional nucleation theory, it is now supposed that some elementary process decreases the strain energy uniformly throughout the entire block.

The time required τ' for $\Delta F(t)$ to become reduced to the order of ΔF_0 may range from τ to a small fraction thereof. In the latter instance the formal theory for τ is essentially no different from the low energy block theory of τ . The nucleation theories recently proposed by DECKER and HARKER,²⁷ BECK⁶⁵ and CAHN⁶⁶ are essentially high energy block theories.

Decker and Harker suppose that the nucleation period is the time required for $\Delta F(t)$ to become substantially less than ΔF_0 , but they propose no explicit form for $\Delta F(t)$. Beck and Cahn have suggested that high energy blocks undergo polygonization and that these polygonized blocks become recrystallization nuclei. Cahn's more detailed theory may be summarized as follows:

- 1 Highly stressed parts of the lattice 'local curvatures' polygonize in a time $\tau' \ll \tau$. On the basis of the evidence that 'weakly' bent single crystals polygonize at the same rate as 'sharply' bent ones it is assumed that τ' is independent of the local curvature ρ .
- 2 During the nucleation period the sub-structure formed by polygonization coarsens and at $t \sim \tau$ elements of the coarsened sub-structure start to grow at the expense of the surrounding matrix. It is assumed that $\tau \propto \rho$ since experimental evidence indicates that, though τ' is independent of ρ , the sub-structure coarsens more rapidly in sharply bent single crystals than in single crystals weakly bent.

In agreement with experience, Cahn's theory requires that nuclei form preferentially at points of highest strain and that the nucleation frequency increase with increasing strain.

The theory also predicts orientations of recrystallized grains whereby they are rotated about an axis in the slip plane and perpendicular to

the slip direction.⁶⁷ Cahn rationalizes exceptions to the Burgers-Louwerse orientation relation in aluminium on the basis of 'pencil glide' whereby slip occurs on any plane containing the [110] direction though the (111) plane is preferred.

In order to explain the acceleration of \dot{N} with time, Cahn assumes that τ is fixed by ρ .^{*} By choosing suitable values of τ (nucleation period for $\rho = 1$) and suitable number distribution curves for potential nucleation sites with respect to ρ , the experimental relations $\dot{N} = f(t)$ can be described satisfactorily.

The major weakness of the theory is the assumption that τ is fixed by ρ or the lack of a theory of substructure coarsening—although the constancy of τ observed by Müller in the recrystallization of rock salt crystals provides some empirical support for the validity of the assumption. Also, no clear explanation is offered for the general equality of $Q_{\dot{N}}$ with Q_G .

By making some plausible assumptions more explicit expressions can be obtained for $\Delta F(t)$ in high energy blocks. First suppose that $\Delta F(t)$ is directly proportioned to the concentration c of dislocations within the block and that c decreases with time according to a radioactive decay law and a suitable sink for the dislocations exists, then:

$$\Delta F(t) = a \exp [-bt] \quad (70)$$

Substituting equation 70 into equation 66 and integrating we have:

$$\tau = a/(\Delta F_0)b \quad (71)$$

In order to calculate τ on the basis of Cahn's theory, it will be assumed without justification that the kinetics of sub-structure coarsening are analogous to the kinetics of normal grain growth in the absence of inclusions and for isotropic σ . $\Delta F(t)$ may then be expressed as:

$$\Delta F(t) = 1/(a + bt^{1/2}) \quad (72)$$

and evaluating τ as before:

$$\tau = 2t^{1/2}/b \quad (73)$$

Though τ is proportional to $t^{1/2}$, the block size D will be virtually a linear function of t for $\tau > (t - \tau)$.

In general the high energy block theory qualitatively accounts for experience excepting that it provides no very plausible explanation for the general equivalence of $Q_{\dot{N}}$ and Q_G . In summary, it appears that a decision on which of the nucleation mechanisms considered is most

* According to conventional nucleation theory, for any homogeneously strained region there is only a probability \dot{N} that a nucleation event occurs in any particular fixed time interval.

likely to operate generally in primary recrystallization cannot be made on the basis of the available experience.

Nucleation in Secondary Recrystallization—There is now fairly convincing evidence that the driving energy for secondary recrystallization is surface energy rather than strain energy. However, the mechanism of nucleation of the process is still no better understood than for primary recrystallization, and, in fact, there is little formal difference between the nucleation theories that have been proposed for the two processes.

According to conventional nucleation theory, nuclei of secondary crystals are formed in small stressed regions that are either retained after primary recrystallization or that are formed by straining deliberately or accidentally after primary recrystallization. However, it seems very unlikely that strains of the order of magnitude ($\epsilon \sim 0.10$ to 0.20) required for conventional nucleation could be retained in the specimen after primary recrystallization.

The block theories for the formation of nuclei in secondary recrystallization are formally the same as for primary recrystallization and the basic equations (64–66) may be used for calculating τ . However, the blocks for primary recrystallization are generally conceived to be sub-grains whereas in secondary recrystallization they are often thought to be entire grains.

Two block theories for secondary recrystallization nuclei that were not given specific consideration in the theory of primary recrystallization have recently attained considerable prominence. These are nucleation *i* due to solution of foreign bodies at grain boundaries and *ii* nucleation due to 'texture inhibition' of grain growth.

Nucleation Due to Solution of Inclusions at Grain Boundaries—Recently BECK, HOLZWORTH and SPERRY⁶⁸ have given a convincing demonstration that the nucleation period in some secondary recrystallization processes can be associated with partial solution of foreign bodies at grain boundaries. According to the qualitative picture, the inclusions hold up the motion of most of the boundaries, but a few grains are either sufficiently large to grow or the density of inclusions on their boundaries are insufficient to retard their growth.

The nucleation period may be associated with the time necessary for the density of inclusions at certain boundaries to decrease to a marked extent. However, an alternative possibility that is amenable to simple treatment is that the dispersion of inclusions is effectively a function of temperature only. In this event we may write (see equation 48)

$$\Delta F_0 = \sigma V(1/D_0 - M) \quad (74)$$

where D_0 is the matrix grain size, M is determined by the dispersion of inclusions and σ is assumed to be isotropic. Assuming that the

RECRYSTALLIZATION AND GRAIN GROWTH

'nucleus' is a grain having a diameter D at time t and D_1 somewhat larger than the matrix grain size at $t = 0$ we have:

$$\Delta F(t) = \sigma V/D \quad (75)$$

It then follows that:

$$\tau = - [(D_0^2/(k\sigma v) (1 - MD_0)^2] \ln [D_1(1/D_0 - M) - 1] \quad (76)$$

Grains capable of serving as nuclei must have an initial size

$$D_1 > D_0/(1 - MD_0)$$

Nucleation Due to Texture Inhibition of Grain Growth—Consider the growth of a crystal into a matrix having a high degree of preferred orientation, such that the interfacial energy σ_m between matrix grains (diameter = D_0) is very small. Under these conditions, the variation of D_0 with time can be neglected. Let σ ($\sigma > \sigma_m$) be the interfacial energy between the secondary crystal or 'nucleus' and the matrix then:

$$\Delta F_0 = \sigma_m V/D_0 \quad (77)$$

and the condition that $dD/dt > 0$ for the growth of the secondary crystal is:

$$D > D_0\sigma/\sigma_m \quad (78)$$

Two theories or a combination thereof may be considered for the nucleation theory. In one it is supposed that secondary crystals of size $D_1 > D_0\sigma/\sigma_m$ are present in the matrix at $t = 0$. Then:

$$\Delta F(t) = \sigma V/D \quad (79)$$

and

$$\tau = - (\sigma D_0^2/k\sigma_m^2 V) \ln [(\sigma_m D_1 - \sigma D_0)/D_0] \quad (80)$$

We may also suppose that secondary crystals arise from isolated aggregates of grains having high energy boundaries and that the initial diameter of the aggregate is somewhat larger than D_1 . Under these conditions $dD/dt < 0$ initially and the form of $\Delta F(t)$ may be assumed to be similar to equation 72. The total nucleation period will be the sum of equations 73 and 80.

In cube texture copper for a mean misalignment between grains of 4° it is estimated, assuming Chalmer's formal relation on lead to be applicable to copper, that $\sigma_m \approx \sigma/2$. Therefore, in order to grow at the expense of the matrix by surface tension forces alone secondary crystals having $D_1 > 2D_0$ must be initially present or must form by some mechanism. For mean misalignment of 1° $D_1 > 5D_0$.

GRAIN GROWTH AFTER RECRYSTALLIZATION

General Observations on the Mechanism of Grain Growth

The growth of a single grain on a polished surface can be followed directly by measuring its diameter at intervals during growth, or by

heating on the microscope stage and following growth continuously. This method has the disadvantage that grain growth is inhibited by a free surface^{38, 69} so that the phenomena observed may not be characteristic of those occurring inside the metal. Grain growth does occur on a free surface, however, and the advantages of direct observation are so great that the method has been used by several workers.

One of the earliest and most detailed series of observations of this type was carried out by CARPENTER and ELAM⁷⁰ in 1920. They used a tin alloy containing 1.5 per cent antimony. This is suitable for such observations, because upon heating to about 150° to 200°C and cooling again to room temperature, the position of the boundary at the elevated temperature remains visible as a thin line upon the surface. Upon reheating and cooling again, a second line is found, corresponding to the new position of the grain boundary. Using this technique, Carpenter and Elam arrived at the following conclusions concerning the mechanism of grain growth:

- a* Grain growth occurs by grain boundary migration, and not by coalescence of neighbouring grains, as two drops of water coalesce.
- b* Boundary migration is discontinuous: the rate of migration of a boundary is not constant in subsequent heating periods, even the direction of migration may change.
- c* A given grain may grow into a neighbour on one side and be simultaneously consumed by a neighbour on another side.
- d* The consumption of a grain by its neighbours is frequently more rapid just as the grain is about to disappear.

Using the same technique and alloy, SUTOKI⁷¹ added the observation that:

- e* A curved grain boundary usually migrates toward its centre of curvature.

By using a statistical technique, HARKER and PARKER⁷² confirmed observation *e* and further observed that:

- f* Where grain boundaries in a single phase metal meet at angles different from 120 degrees, the grain included by the more acute angle will be consumed, so that all angles approach 120 degrees.

Many of these points are illustrated by the series of photographs presented in *Figure 21*.⁷ The metal is zinc, heated on the stage of the microscope and examined with polarized light, so the positions of the boundaries can be followed continuously. The white lines represent positions of the grain boundaries at an earlier stage of growth, and should be disregarded. The upper white grain marked X remained essentially unchanged for the first 30 minutes of heating except for

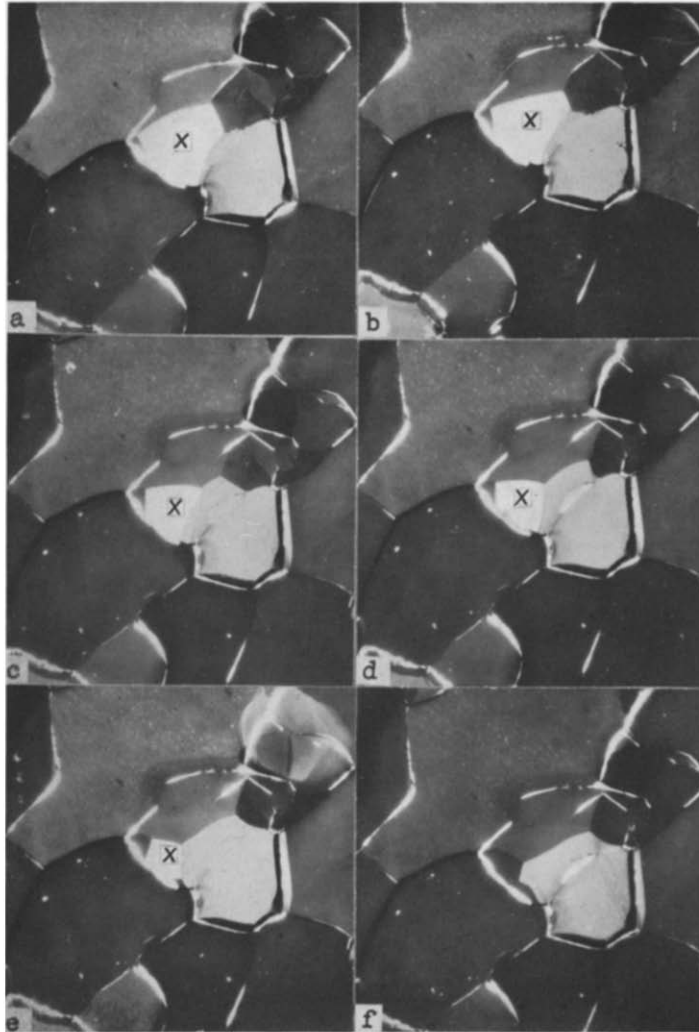


Figure 21. Grain growth in zinc observed with polarized light on a hot stage at about 200°C : the white grain marked *X* is gradually being consumed:
 a 0 min; b 30 min; c 37 min; d 38 min; e 40 min; f 42 min

slight migration of the curved boundary on the right as shown in *Figures 21a* and *21b*. Suddenly after 36 minutes the grains to the right and left grew in, changing X from a four sided to a three sided grain. The configuration was then more unstable, and the acute corner of the grain was slowly consumed and finally the whole grain disappeared (*Figure 21f*) after 41 minutes.

An additional observation on the mechanism of grain growth is pertinent. When a two component alloy is heated slightly above the solidus, melting starts at the grain edges and grain faces. Since the metal is now hotter than before one would expect grain growth to occur more rapidly, instead it stops completely.⁴⁰ In similar specimens heated to temperatures just below the solidus grain growth continues, and it will commence again in the partially melted specimens if they are cooled below the solidus temperature.

Driving Force for Grain Growth—Two different sources of decrease in free energy have been proposed as the driving force for grain growth after recrystallization. The first originally suggested by CZOCHRALSKI⁷³ postulates that the grains formed by recrystallization have residual strain energy, and that upon further heating the more perfect ones will grow at the expense of the less perfect ones. The second, suggested first by EWING and ROSENHAIN,⁷⁴ considers the interfacial energy of the grain boundaries to be the driving force for grain growth.

Many of the observations on the course of grain growth may be explained by the assumption that the driving force is a difference in residual strain energy between the grains, as it is in recrystallization. This assumption is refuted, however, by the fact that grain boundary melting stops grain growth. If the driving force were a difference in energy between adjacent grains, the mere interposition of a liquid layer would still permit grain growth to occur by the solution of the more strained grains in the liquid, and the redeposition of material from the liquid on the less strained grains.

The evidence supports the conclusion that the driving force is the surface tension of the boundaries. Numerous authors^{75, 76} have pointed out that the shapes of metal grains are identical with the shapes of cells in foams: this would indicate that surface tension controls the shape of metal grains as well as the shape of foam cells. SMITH⁷⁷ has demonstrated that in a soap foam surface tension can lead to cell growth that simulates grain growth in metals. If the foam is prepared in a partially evacuated container, gas can diffuse across the cell walls from the convex to the concave side. Thus the boundaries migrate toward their centres of curvature exactly as in grain growth, foam cells disappear and the average cell size increases.

VOGEL⁷⁸ and more recently BRAGG⁷⁶ and HARKER and PARKER⁷² have pointed out that the boundaries between undistorted grains should

behave as if they had a surface tension. Atoms on the concave side of a curved surface are more completely surrounded by atoms of their own crystal than atoms on the convex side. Thermal motion causes atoms at the curved interface to move continuously from one surface to the other, and since they are more stable on the concave side, there will be a net flow of atoms to this surface. Thus the boundary will migrate towards its centre of curvature. Similarly, if the surface tension of all boundaries is equal, where three boundaries meet at a point at an angle of other than 120 degrees, the atoms on the grain included by the most acute angle will be less surrounded and less stable than those on other grains. The net flow of atoms will lead to the consumption of the grain included by the more acute angle. DUNN and co-workers^{37, 58} and CHALMERS and co-workers⁵⁹ have made use of these concepts to measure the relative surface energies of intersecting boundaries whose surface energies are different.

The effect of grain boundary melting on the rate of grain growth may be explained in terms of the surface tension theory as follows:⁴⁰ the driving force for grain growth due to surface tension will be:

$$\Delta F = \sigma V \left(\frac{1}{r_1} - \frac{1}{r_2} \right) \quad (81)$$

where V is the atomic volume, σ is the surface tension, and r_1 and r_2 are the radii of curvature of the grains between which matter is transferred. In a solid metal, since there are no voids at the grain boundary:

$$r_1 = -r_2 \quad (82)$$

Thus

$$\left(\frac{1}{r_1} - \frac{1}{r_2} \right) = 2 \left(\frac{1}{r_1} \right) \quad (83)$$

Now, if melting occurs at the grain boundaries, r_1 need not equal $-r_2$. Near grain edges, as shown in *Figure 22*, r_1 may have the same sign as r_2 if some melting has occurred, thus $\left(\frac{1}{r_1} - \frac{1}{r_2} \right) \ll \left(\frac{1}{r_1} \right)$ and the rate of growth will be markedly reduced.

It is interesting that even if melting is confined to the region near grain edges, grain growth will stop. This probably results from the fact that the curvatures near grain edges are more pronounced than in the centres of grain faces. When a new three grain junction is formed during grain growth, it will not in general have the equilibrium configuration. The adjustment of the interfacial angles to the correct value will introduce strong curvature into the grain faces, near the edges. These will gradually smooth out over the grain face, but since new junctions are continuously forming, the smoothing may not go to completion.

In view of the foregoing and much other evidence, there can be little doubt that the driving force for grain growth after recrystallization is the surface energy of the grain boundaries, and this driving force will be assumed in the arguments which follow.

Geometry of Grain Growth—A polycrystalline metal consists of an assemblage of polyhedra in contact along faces, edges and corners. To simplify this discussion, only a two-dimensional array of grains will be considered; these will be in contact along faces and edges, and it will be assumed that the surface tension of all boundaries is equal. In such an array of cells or grains, with only three grains meeting at one point, the average number of sides for a grain is six, but there is a distribution, with grains being found which have from three to nine, ten or even more sides. If all the cells had exactly six sides, it would be possible for each set of three grain boundaries to meet at a point at angles of exactly 120 degrees, even though the grain sizes were not uniform, and for all the grain sides to be straight. As Harker and Parker point out,⁷² this would be a stable array, and there would be no tendency for the grain boundaries to migrate. However, if a grain is introduced with only five sides, it is geometrically necessary to introduce one with seven sides, so that the average number remains at six. Neither the five nor the seven-sided grain will have straight sides if the boundaries meet at angles of 120 degrees. Grains having less than five sides will have their faces concave inwards, while those having more than five sides will have their faces concave outwards. As a result of these curvatures, the grains with less than six sides will tend to grow smaller, and the grains with more than six sides will tend to grow larger.

For much of the time the boundary migration is continuous, but occasionally a grain gains or loses a side, then the rate of motion is discontinuous. There are only two fundamental mechanisms by which the number of sides change⁷⁹ in two dimensions. As shown in *Figure 23*, where four grains meet, two of them have a side in common, and the other two are separated by the common side of the first two. As a result of boundaries migrating toward their centres of curvature, the two separated grains approach each other until finally all four boundaries meet in a point. Further boundary migration brings the two separated grains into contact, causing each of them to gain a side, and separates the two grains which were originally in contact, causing

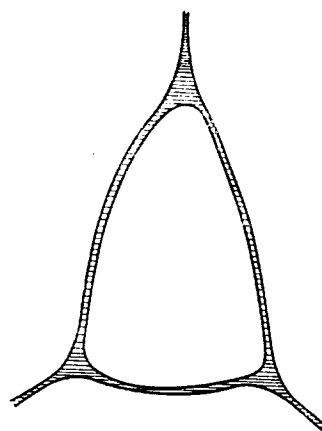


Figure 22. Change in shape at a grain boundary as a result of the grain boundary melting

each of them to lose a side. As a result of changes like this, four-sided grains can change to three or less often to five, five sides go with about equal frequency to four or six, while six-sided grains can go to five or seven. If a three-sided grain appears, it usually disappears directly, with the loss of a side by each of the grains with which it was in contact. It is only when a three-sided grain disappears that grain growth can be detected by a counting technique.

Changes of this type would not occur in a perfect froth where all the grains had six sides, but in practice, one never finds such a froth or such a metal. The introduction of even one grain with a non-equilibrium shape upsets the balance of the whole system, and it cannot be restored in general, because as boundaries migrate in a direction to restore the equilibrium configuration, grains disappear so the non-equilibrium configuration is self-perpetuating. Thus occurs grain growth.

Formulation of Continuous Grain Growth—An expression for the rate of grain boundary migration where the surface energy of the boundary is the driving force has been presented as equation 39. For isothermal conditions, this may be simplified to

$$G = K' \sigma V / r \quad (84)$$

where v is the gram atomic volume, G is the rate of grain boundary migration, σ is the surface energy of the boundary, r is the radius of boundary curvature, and the rate constant K' varies with temperature according to the relationship.

$$K' = K'_0 \exp (- Q_G / RT) \quad (85)$$

To develop from this an expression for the rate of grain growth we shall make some simplifying assumptions about the nature and geometry of the process. Later, these will be tested with a model. It will be assumed that the boundary surface tension, σ , is independent of grain size or amount of grain growth, and that the efficacy of inclusions in retarding grain growth is independent of temperature and grain size. Secondly, it will be assumed that

$$r \propto D \quad (86)$$

where D is the average diameter of the grains present. Thirdly it will be assumed that

$$\frac{dD}{dt} \propto G \quad (87)$$

Thus, from equation 84 we may write

$$\frac{dD}{dt} = \frac{K \sigma V}{D} \quad (88)$$

Integrating and evaluating the integration constant at $t = 0$

$$D^2 - D_0^2 = K\sigma Vt \quad (89)$$

where D_0 is the grain size at $t = 0$. If D_0^2 is negligible compared to D^2 , as it is when much grain growth has occurred, this simplifies to

$$D = (K\sigma Vt)^{1/2} \quad (90)$$

Equation 89 predicts that if the logarithm of the average grain diameter, D , is plotted as a function of the logarithm of time a straight line with a slope of 0.5 should be given if D_0 is sufficiently small to be neglected.

FISHER⁸⁰ has reported that D is proportional to $t^{1/2}$ for the growth of soap foam cells in a partially evacuated container. In this case, the rate of boundary migration is controlled by diffusion of gas through the cell walls which like the rate of atom transfer across boundaries is proportional to the curvature of the cell walls. Similarly, the driving force for the diffusion is the surface tension of the cell walls, so the system makes a good model for grain growth in metals. The fact that $D \propto t^{1/2}$ indicates that the geometrical analysis is essentially correct.

Quantitative Observations of Grain Growth

Grain sizes are usually determined by counting the number of grains in a unit distance or area, on a polished surface, and are expressed as the average grain diameter. This measuring method reveals nothing about grain size distribution, and will reveal grain growth only when it has proceeded to the point where some grains have disappeared.

For engineering work it is customary to present isochronal growth curves, showing the increase in grain size with increasing annealing temperature for a constant heating time. Isothermal data, where the grain size is measured as a function of time, gives a better picture of the process, however. If the grain size is plotted directly against time, isothermal curves appear to indicate that growth stopped after relatively short annealing times, when grain sizes which appear to be characteristic of the temperature are attained. The time dependence of grain size is shown better by plotting the logarithm of the average grain diameter as a function of the logarithm of time (*Figure 24*), since this gives a nearly linear relationship, as indicated above. When grain growth curves are mentioned in the following discussion, the reference

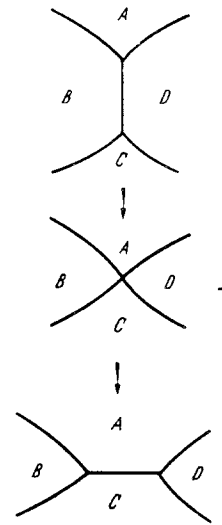


Figure 23. Changes in grain boundary configuration which occur during grain growth

will be to logarithmic plots of this type. First we shall present and discuss examples of continuous growth. Under many conditions the grain size does not remain uniform during growth; these cases of discontinuous growth will be presented later.

Isothermal data on the course of continuous grain growth have been obtained for relatively few metals. In most cases, the data may be represented by an equation suggested by BECK and his co-workers:^{38, 32}

$$D = Kt^n \quad \dots (91)$$

This equation applies reasonably well if the grain size is large compared to the initial grain size and small compared with the limiting grain size imposed by inclusions.

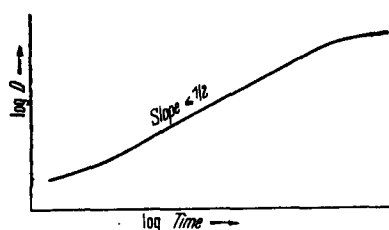


Figure 24. Typical isothermal growth curve for continuous grain growth (schematic)

It is equivalent to equation 90 if $n = 1/2$, but as will be seen, the measured values of n usually are much less than $1/2$. A wide range of values for the exponent have been found, assuming that equation 91 applies. Beck, Kremer, Demer and Holzworth, who first used this method of plotting,³⁸ found that the exponent increased from about

0.09 at 400°C to 0.32 at 600°C in high purity aluminium. In an aluminium alloy containing 2 per cent magnesium they found the exponent varied from 0.17 to 0.45 over the same temperature range. In 70 : 30 α -brass of commercial purity, both BECK³² and BURKE³⁹ found the exponent to be independent of temperature, with a value of about 0.2. On the other hand, BURKE⁴⁰ found that in very high purity α -brass, the exponent increased from about 0.35 to a little over 0.5 over a temperature range of 500° to 850°C, with the value increasing with temperature. MILLER³³ has studied grain growth in a number of carbon steels between 815° and 1,250°C and reports values for n ranging between 0.08 and 0.22.

Temperature—As indicated previously, the temperature dependence of the rate of grain growth should be given an equation of the type:

$$G = A \exp (Q_G/RT)$$

Values of Q_G the activation energy for grain growth, as determined by several workers are listed in Table VII.

No single activation energy can be computed from the growth curves obtained for aluminium, and the aluminium-magnesium alloy studied by BECK and his co-workers,³⁸ because the growth law changed with temperature. Nevertheless the rate of growth increased with increasing temperature approximately as rapidly as for the metals

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Table VII. Values of the activation energy for grain growth Q_G

Metal	Q_G kcal/gm atom	Observer
Brass* ..	60	Burke ³⁹ Walker ^{39, 44}
Brass* ..	62	Beck ⁸²
Brass† ..	40	Burke ⁴⁰
Tungsten ..	110	Robinson ⁸⁴
γ -Iron‡ ..	90-113	Miller ⁸³
α -Iron§ ..	110	Burke and Chandler ⁸⁵

* Commercial purity

† High purity

‡ Various commercial carbon steels

§ Westinghouse puron-deoxidized

where an activation energy can be computed. Actually, the activation energies reported for α -brass of commercial purity apply only over the temperature range of 500° to 750°C. Above that temperature the rate increased more rapidly than would be indicated by the activation energy reported. Other experiments indicated that at least part of the increase in rate resulted from the solution or coalescence of growth inhibiting inclusions, and it is of course possible that a similar solution or coalescence contributes to the increase in rate observed with all the other metals. This is discussed more fully in another section.

Composition—The effect of composition on grain growth is obscure and few specific experiments have been performed to elucidate the effect. It seems to be generally true that alloys have a greater tendency to display continuous grain growth than pure metals. Aluminium, iron, zinc and even spectroscopically pure copper, all show exaggerated growth with the development of mixed grain sizes. On the other hand, it is not possible to cause such exaggerated growth in brass even by slightly straining the specimen before annealing. In aluminium, this procedure produces such exaggerated growth that single crystals are manufactured this way. The addition of small amounts of silver to high purity zinc permits continuous growth to occur.³³ In this case the effect of silver is to retard grain growth at low temperatures. At higher temperatures growth occurs so slowly that the inclusions responsible for low temperature discontinuous growth dissolve before much growth has occurred.

Beck, Kremer, Demer and Holzworth investigated the relative rates of grain growth in high purity aluminium and in an aluminium magnesium alloy.³⁸ They found that the rate of growth was greater in the pure metal at small grain sizes, but as the grain size increased

the curves crossed, so that at coarser grain sizes, the rate of growth was greater in the alloy.

Limiting Grain Sizes—There has been much confusion concerning how large the grain size in a metal may become with prolonged heating. Grain sizes for engineering use are frequently reported as a function of heating temperature for a constant heating time. Since the grain sizes determined in this way are relatively insensitive to heating time when it is of the order of one hour, the impression has grown that these grain sizes are characteristic of the heating temperature. On the other hand, the formulation of grain growth just presented, and many of the growth curves indicate that grain growth should continue indefinitely until the specimen becomes a single crystal. Actually, there does seem to be a limiting grain size which is characteristic of the specimen material and the temperature, but in most cases it is larger than the grain size attained after relatively short heating times. This fact was well known to JEFFRIES,⁸⁶ who pointed out that the final sizes may be attained after a few minutes heating at high temperatures.

There are two important reasons why grain growth may stop before the piece becomes a single crystal. The first arises from the fact that grain growth is inhibited by a free surface.^{38, 69} A striking example of this has been reported by Beck and his co-workers who found that in sheet specimens, continuous grain growth stops when the average grain size approximates to the thickness of the specimen. Similarly, in wires, it is not possible to grow grains having a dimension greater than the diameter of the wire by continuous growth. If the specimen is large, however, growth will stop before the grains approximate the dimensions of the piece. This results from the inhibition of grain boundary migration by inclusions.

Since the early work of Jeffries on the effect of thoria on grain growth in tungsten,⁸⁶ metallurgists have recognized that second phase inclusions inhibit grain growth. It is not necessary to have a continuous layer of a second phase at the grain boundaries, in fact, the more highly dispersed the second phase is, the more effective it will be in preventing growth. An example of how second phase inclusions can interfere with growth is shown in *Figure 25*. The points of the scallops on the boundary are points where the boundary is being held back by inclusions.

An excellent example of the effect of second phase inclusions on grain growth has been presented by BECK, HOLZWORTH and SPERRY.⁶⁸ The aluminium alloy they used contained 1.1 per cent manganese and a manganese-aluminium phase is present at 550°, 600° and 625°C but is completely dissolved at 650°C. Below 650°C a limiting grain size characteristic of the temperature is quickly reached, and no further grain growth occurs. Above that temperature, continuous grain



Figure 25. Inclusions in α -brass retarding grain boundary migration

growth occurs in the absence of inclusions, and proceeds until a large grain size is attained.

Burke found similar results in a 70 : 30 α -brass.⁴⁰ A limiting grain size of 0.55 mm at 800° and of 0.75 mm at 850°C was found in a brass of commercial purity, which contained a number of inclusions. In brass of exceedingly high purity, the limiting grain size was about 1.75 mm at only 800°C, and the specimen thickness was only a little larger than this. Had a larger specimen been available, even more grain growth might have occurred.

The increase in limiting grain size with increasing temperature may result from either the solution or coalescence of growth inhibiting inclusions. For this reason the course of grain growth in an inclusion bearing material may be influenced by prior heat treatments that control the dispersion of inclusions. In the brass of commercial purity just described, the grain growth rate could be increased by as much as fifty times by heating the specimen to 850°C and slowly cooling,⁴⁰ so that the inclusions were coalesced prior to the final working.

Rationalization of Grain Growth Observations

There are many factors which may contribute to decrease of the slope of isothermal logarithmic growth curves, so that the exponent n in equation 91 is less than 0.5. As equations 89 and 90 indicate, one would expect the slope to be 0.5 only in cases where D_0^2 is negligible compared to D^2 . If it is not negligible, the slope of the $\log D/\log t$ curve will be lowered, and in many of the published data, particularly those obtained at low temperatures after small amounts of grain growth, this explanation may apply.

Equation 89 indicates that grain growth will continue until the specimen becomes a single crystal. Grain growth may stop while the grain boundaries are still curved, however, either because the average grain size approximates the thickness of the specimen, or because inclusions prevent further growth. In the latter case, SMITH⁷⁷ has reported a computation by Zener which indicates that the limiting grain size should be given approximately by the expression:

$$D_l = d/f \quad (92)$$

where D_l is the limiting grain size, d is the average diameter of the inclusions and f is their volume fraction. Under these conditions, the rate of growth will be controlled not by the average grain size present, but by the difference between this grain size and the limiting one, so that assuming that D_l is independent of time and temperature:

$$\frac{dD}{dt} = K \left(\frac{1}{D} - \frac{1}{D_l} \right) e^{-\left(\frac{Q_d}{RT}\right)} \quad (93)$$

where K is equivalent to $(K\sigma V)$ of equation 88. Integrating and evaluating the integration constant at zero time, one gets:

$$\left(\frac{D_0 - D}{D_i}\right) + \ln\left(\frac{D_i - D_0}{D_i - D}\right) = \frac{K}{D_i^2} t \exp(-Q_G/RT) \quad \dots (94)$$

By experimentally determining Q_G , K and D_i , the isothermal growth curve can be computed for comparison with experimental results.

In Figure 26 a series of curves computed in this way for very high purity brass⁴⁰ are shown. A value of 40 kcal/gm atom was used for

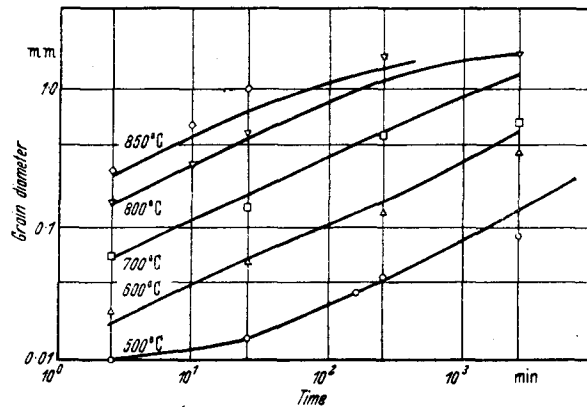


Figure 26. Comparison between grain growth data obtained with high purity brass and curves calculated using equation 93

Q_G , 5.31×10^5 cm/min for K and the experimentally determined values of 0.005 mm for D_0 and 1.75 mm for D . The general agreement with the points plotted is excellent and would have been improved if the temperature dependence of D_i had been taken into account. Equation 94 does not fit grain growth curves in general. The shape of the curves is the same but the slope is usually found to be less than predicted. There are many possible interpretations of this discrepancy. They cannot be discussed quantitatively but it seems worth while to mention several of them and point out the direction in which they will operate.

If inclusions are present, the rate may be controlled solely by the rate of coalescence of the inclusions; in this case, the dependence on time is not yet clear. There is the further possibility that mobile inclusions may collect preferentially on grain boundaries by diffusion during grain growth. This will be more probable when the grain size is large and the boundaries are moving slowly. Thus, the inclusions will become increasingly effective as the grain size increases, and the slope of the growth curve will be decreased.

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The surface tension of the boundaries may decrease with time. This may result from a change in texture or as Benedicks suggests⁷⁵ by diffusion of soluble impurities to the boundaries. This latter effect will become more pronounced as the rate of grain growth decreases, and will operate to decrease it further.

Changes in the distribution of grain sizes and interfacial angles can also change the rate of grain growth for a given average grain size, although they will not influence the rate of migration of a boundary of given curvature. Equations 89 and 90 were derived with the assumption that the grain size distribution and the grain boundary configuration is independent of the average grain size. Only under these conditions, does a constant proportionality exist between average grain size and average boundary curvature. If the grain size distribution becomes more uniform during grain growth, the smaller grains with more highly curved faces must be disappearing preferentially. The average radius of curvature of the grain faces present will thus increase more rapidly with increasing grain size than the average grain size, thus the rate of growth will decrease more rapidly than would otherwise be predicted. The rate of growth itself, of course, will be greater than would be predicted, because the migrating boundaries are more curved than they would be in a specimen having an equivalent uniform grain size.

Harker and Parker have shown that the interfacial angles may approach more closely to 120° as growth proceeds.⁷² If this is so, the condition of geometrical similarity at all grain sizes is not met, and in effect the average radius of curvature of the grain boundaries will be decreasing more rapidly than the average grain size, so the slope of the $\log D/\log t$ curve will be decreased.

Effect of a Free Surface—In a three dimensional array of grains, grain faces must extend from one three grain junction to another. The marked curvatures about two axes introduced by this requirement, will cause relatively rapid boundary movement. If on the other hand, the grains are two dimensional and extend completely through the piece, the face edges in contact with the surface can adjust their positions so the grain faces have simple cylindrical curvatures, thus the driving force for grain growth and the rate of grain growth will be much reduced. The increase in effective radius of curvature when the grains become two dimensional may be sufficient for the inclusions present to prevent any further grain growth.

This would indicate that in sufficiently thin sheets, even two dimensional grains should have sufficient boundary curvature to permit some growth. Burke studied this and found that in brass, the ratio of limiting grain size to sheet thickness increased with decreasing sheet thickness,⁴⁰ as predicted by the above explanation.

Secondary Recrystallization

Thus far, discussion has been confined to cases of continuous grain growth where the grain size increases uniformly after primary recrystallization. Under some conditions, primary recrystallization results in a fine grained structure which does not coarsen much upon further heating at a low temperature. As the temperature is raised, 'secondary recrystallization' may occur. Some grains start to grow after a nucleation period, and these rapidly growing grains consume their stable smaller neighbours. The kinetics of the process are apparently identical to those of primary recrystallization and have been treated in an earlier section. The driving force appears to be the surface tension of the boundaries as it is in ordinary grain growth, since the process will occur in the absence of deformation. Nevertheless, slight deformation may decrease the nucleation period, and promote the appearance of secondary recrystallization. Burgers has reviewed the results of a number of investigations of these phenomena, and more recent work has been reported by BECK, HOLZWORTH and SPERRY,⁶⁸ KRONBERG and WILSON,⁸⁷ WARD,²⁵ TURKALO and TURNBULL⁸⁸ and ROSI and ALEXANDER.²⁶

A necessary condition for the occurrence of secondary recrystallization is the inhibition of growth of the grains that results from primary recrystallization. Two mechanisms for this inhibition are well established: a proper dispersion of a second phase, or the presence of a marked preferred orientation.

Inclusion Inhibited Growth—Exaggerated grain growth in the presence of growth-inhibiting inclusions was first observed by Jeffries in thoria bearing tungsten wire.⁸⁶ He found that the coarsening temperature increased with increase in the thoria content until a thoria content was reached at which no growth at all occurred. Beck, Holzworth and Sperry studied aluminium alloys containing a dispersed manganese-aluminium phase.⁶⁸ They found that exaggerated growth occurred only at a temperature at which the manganese-aluminium phase was almost completely in solution. Below this temperature, little or no grain growth occurred. Above it, continuous growth took place. They also observed a nucleation period for the onset of the phenomenon which increased with temperature, and with decreasing amount of the second phase.

An important consequence of such exaggerated growth is that the limiting grain size is controlled only by the number of nucleation centres, and not at all by the number of inclusions or the dimensions of the specimen as in continuous growth. In fact, thin sheet specimens may be transformed to single crystals by secondary recrystallization. A common example of discontinuous growth, which is not so

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pronounced as the cases cited, is the sudden coarsening of deoxidized steels, at a quite definite coarsening temperature.

Texture Inhibition—Similar discontinuous growth may occur in specimens with strongly preferred crystal orientations. An outstanding example is the secondary recrystallization of cube-texture copper. The growth of the as-recrystallized grains is slow, because, as Beck has suggested, grain boundaries between grains of nearly the same orientation migrate only with difficulty. The origin of the secondary grains is not clear, but there is a well defined nucleation period.

A striking fact is that the new grains have well-defined orientations with respect to the matrix—as Bowles and Boas⁵⁷, and Kronberg and Wilson⁸⁷ have reported, most secondary grains have an octahedral pole in common with the matrix, but are rotated about this pole by approximately $\pm 30^\circ$.

RECRYSTALLIZATION TEXTURES

Two fundamentally different mechanisms for producing a preferred orientation by recrystallization will be considered. The first—the ‘oriented nucleation’ hypothesis—almost universally accepted until recently, postulated that the orientation of the recrystallized grains is controlled exclusively by the orientations of the recrystallization nuclei. The other, suggested most recently by BECK,³⁵ assumes that recrystallization nuclei may be randomly oriented, and that a selection is made among these by the orientation dependence of their growth rates. Thus the orientations found in the recrystallized metal will be those which were most favourably oriented for growth in the deformation texture. This will be termed the ‘oriented growth’ hypothesis. Since textures in non-ferrous metals have already been discussed in Volume I⁸⁹ of this series, we will concern ourselves here primarily with a discussion of the evidence favouring these two mechanisms of forming recrystallization textures in face-centred cubic metals.

From studies of the orientations of recrystallized grains in deformed aluminium single crystals, BARRETT⁹⁰ and others have reported that the new grains definitely have orientations which differ from that of the grain from which they grew. He pointed out that the orientation relationship was reasonably consistent in many cases with a rotation about axes of the type [111] which the new and old grains held in common. Since that time a great deal of evidence has accumulated which indicates that this relationship frequently obtains. It has been observed in the secondary recrystallization of cube-texture copper,^{56, 87} after the recrystallization of deformed brass,⁹¹ and copper⁹² and aluminium³⁵ single crystals.

In all cases, the magnitude of the rotations involved are reasonably

constant, they vary between 20 and 40 degrees. KRONBERG and WILSON⁸⁷ report that when two close-packed planes of atoms are rotated about a common normal, there are several specific rotations which place a number of atoms in each array in coincidence. Specifically, for rotations of 22 or 38 degrees, the coincidence sites lie on a hexagonal array with a parameter $\sqrt{7}$ times that of the primitive array. It might be pointed out that in these cases, rotations in opposite directions which total 60 degrees lead to two new orientations which are twins, thus a rotation of minus 22 degrees gives a twin of a plus 38 degree rotation. Kronberg and Wilson report that these rotations of 22 and 38 degrees most accurately describe the orientation relationship they observe in the secondary recrystallization of cube-texture copper.

BECK and HU³⁵ studied the relative rates of growth of grains having a number of different orientations by scratching the polished surface of a deformed single crystal and then heating it. They observed that grains having many orientations appeared along the scratch, but that those related to the parent by approximately a 30 degree rotation about a common octahedral pole grew most rapidly. They thus suggested that even if many orientations were nucleated, only those close to this most favoured orientation would appear in the recrystallized metal, and that the recrystallization textures can be accounted for solely on the basis of oriented growth.

While it is undoubtedly true that oriented growth must provide in this fashion a selection between favourably and unfavourably oriented nuclei, and must thus contribute to the formation of recrystallization textures, there are other observations that indicate that a nucleation is not completely random. If the orientations of recrystallization nuclei were completely random, then oriented growth would select all of those which had crystallographically similar orientations with respect to the matrix. Because of crystallographic symmetry, one would expect to find recrystallized grains appearing in face-centred cubic metals which were related by rotations about each of the four $[111]$ directions and rotated in either direction about these axes. If the rotation is taken to be about 30 degrees, as Beck and Hu report, then this would give rise to eight new orientations—four sets of twins—corresponding to two possible rotations about each of four $[111]$ axes. In the Kronberg–Wilson rotation, sixteen new orientations should be observed, corresponding to rotations in either sense by either of two possible amounts about four axes.

All of these possible new orientations are rarely if ever observed but certain of them seem to appear reproducibly following the same treatment. This could only result from the formation of nuclei having a limited number of orientations. For example, in the recrystallization of cube-texture copper, Kronberg and Wilson find that, with one

exception in 63 observations, the 22 degree rotations occur only in a clockwise fashion about the north west and south east $[111]$ poles of the cube texture: the rolling direction corresponding to north. The 22 degree rotations are counter clockwise about the north east and south west poles. All 38 degree rotations are opposed to the 22 degree rotations.

There is also evidence to indicate that the new grains may be related to the parent by rotation about only a reproducible few of the possible four $[111]$ poles. MADDIN, MATHEWSON and HIBBARD⁹¹ found that upon recrystallizing deformed single crystals of brass, the new grains were related by rotations about the poles of the octahedral planes upon which slip occurred, and about no others. Similar observations have been made in copper by BECKER⁹² and by one of us.⁹³ The deformation fibre texture of aluminium wire has a $[111]$ axis parallel to the wire axis and that does not change upon recrystallization. BECK⁹⁴ has pointed out that even though the new grains had different orientations from their parents, if they were all related by rotations about an appropriate $[111]$ direction, the new texture would be indistinguishable from the old. Here, however, only one of the four possible axes are chosen. Had the new grains been related by rotations about all of the $[111]$ axes, a much more random texture would have been obtained.

Similarly, the recrystallization texture of rolled aluminium differs only slightly from the deformation texture. BECK and HU⁹⁵ have explained this by a similar rotation. The deformation texture of aluminium consists of two pairs of orientations, only one of which is shown in Figure 27. The two halves of the pair are related by a rotation of approximately 40 degrees about an octahedral pole, A , which they have in common. If the new grains are related to the old by rotations in the correct direction about this pole, the halves of this component of the texture interchange, and the new texture will be indistinguishable from the old. If pole B is chosen for the rotation, a rotation of about 40 degrees will transpose the deformation texture into the well-known cube texture. Beck and Hu find traces of the cube texture in the recrystallized aluminium, and have microscopic evidence that the first

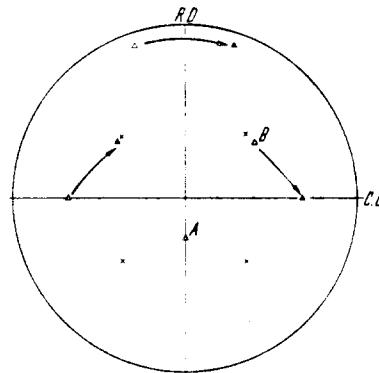


Figure 27. Derivation of recrystallization texture from deformation texture in aluminium by rotation about $[111]$ directions: \times shows cube texture positions, \triangle and \blacktriangle are different components of the deformation texture

mentioned reorientation does in fact occur. While the new textures can be explained in terms of a rotation about a $[111]$ pole, not all such poles are used, nor are rotations of both senses used. Again it seems necessary to assume that while some selection of orientations may have been made by oriented growth, only a limited number of orientations were produced at the time of nucleation.

There is little information to guide speculation on what controls the orientation of the nuclei. None of the theories of nucleation previously described predict the observed orientation relationships. The work of Maddin, Mathewson and Hibbard, and of Becker, indicates that the deformation process itself may control this orientation. In this connection it is interesting to note that HEIDENREICH and SHOCKLEY⁸⁶ have reported that deformation seems to produce some rotation about the normal to the (111) plane on which slip occurs. Similarly, Barrett reported⁹⁰ that the spread of orientations in a compressed aluminium single crystal could be explained by a rotation of about 10 degrees in either direction about the $[111]$ poles which were perpendicular to the $[011]$ compression axis.

Decker-Harker Theory—A completely different mechanism for the production of recrystallization textures has been proposed by DECKER and HARKER⁸⁴ and seems to be supported by experimental evidence in the case of silicon ferrite. The recrystallization texture of silicon ferrite is $(110)[001]$. Harker and Decker have demonstrated by direct x-ray studies of deformed coarse grained specimens that grains in the starting material which have this orientation are more distorted by a given reduction in thickness than grains having other orientations. Microscopic observation shows that deformed grains having these orientations also recrystallize first upon heating. However, they find that the orientations of the recrystallized grains are essentially the same as the orientation of the parent. Apparently this is a case of recrystallization *in situ*, a gross case of polygonization. Decker and Harker propose that in a fine-grained specimen, these recrystallized, strain-free grains will grow at the expense of the deformed matrix, and produce a recrystallized texture of this orientation. This does not happen in the very coarse grained material upon which the observations were made, because the distances involved in growth are too great, but it seems a reasonable process to occur in a fine grained material. It should be noted that the theory provides a mechanism for producing a recrystallization texture in a deformed material that does not have a well-defined deformation texture.

ANNEALING TWINS

One of the most prominent features of recrystallized face-centred cubic metals are the familiar annealing or recrystallization twins. These

usually appear as parallel-sided bands that run across grains; the parallel boundaries coinciding with (111) twinning planes. The structure is coherent across these boundaries, that is both parts of the twin hold a single (111) plane in common. Non-coherent boundaries also appear where a twin terminates within a grain, or where steps occur along a coherent boundary. At these composition surfaces a (111) plane is not held in common by both halves of the twin.

It is well known that the face-centred cubic structure may be formed by stacking close-packed layers of atoms (which are (111) planes) in the sequence *ABCABC*. A face-centred cubic twin may be formed by stacking in the sequence *ABCBA*. This sequence also forms a close-packed structure in which the distance of closest approach of atoms is unchanged, but the right half is the mirror image of the left half. The C plane indicated by underlining is held in common by both parts of the twin.

Mechanism of Twin Formation—The mechanism proposed for the formation of annealing twins follows the concept that a change in stacking sequence is all that is necessary to form an annealing twin. This hypothesis was first presented by CARPENTER and TAMURA.⁹⁷ BURKE⁹⁸ obtained evidence that this mechanism must operate, and FULLMAN⁹⁹⁻¹⁰³ has described auxiliary conditions necessary for its operation and has measured the surface tension of twin interfaces.

The change in stacking sequence necessary for the formation of an annealing twin may occur whenever a properly oriented grain boundary migrates. If the interface corresponds approximately to a (111) plane in the growing crystal, growth will proceed by the deposition of additional (111) planes in the stacking sequence *ABCABC*. Each newly added plane has of course the choice of two positions, but if the structure and orientation are to be maintained, this stacking sequence must be followed. If the newly deposited layer falls in the wrong set of positions so the sequence is *ABCABCB*, the first layer of a twin would be formed. This would not be difficult from an energy point of view, since coherent interfaces have very low surface energies and the number of nearest neighbours is unchanged by such a stacking error. Once a twin interface is formed, further growth may continue with the sequence in reverse order, *ABCABCBACBA*, forming a twin. A second accident of the same type at a later time on a parallel (111) plane will form a parallel twin interface and restore the original orientation. A twin band will now exist. If the accident occurs on a non-parallel (111) plane of the twin, the original orientation will of course not be restored, rather a second order twin of the original orientation will be produced. Such second-order twins are observed with reasonable frequency.

The growth accident may be expected to occur particularly when a

discontinuous change takes place in the nature of the matrix being consumed. One possible discontinuity is a twin fault* which provides a ready-made nucleus for an annealing twin. However, all of the annealing twins found even in freshly recrystallized metal cannot be nucleated in this way. Recrystallized grains almost always have a different orientation from the parent grain although frequently the parent and daughter grains have an octahedral plane in common. Although twin faults may exist on several (111) planes in the parent, only those on a common octahedral plane can nucleate annealing twins in the daughter grain. Thus by this mechanism, one can account for only one family of annealing twins in a given grain, although several are frequently observed.

A second type of discontinuity may be found when a grain gets a new neighbour either during recrystallization or grain growth, and it will permit the formation of an annealing twin on any possible plane in the growing grain. Grain growth occurs by the repetition of transformations like that shown in *Figure 23*. Grain *A* which was originally in contact with grains *B* and *D* at a single corner, gains a side so that it is now in contact with grains *B* and *C* at one corner and with grains *C* and *D* at another corner. When this transformation occurs, a twin may be formed in one of the four new corners, as shown in *Figure 28b*. This is in agreement with the observation that new twins appear to form frequently in grain corners.

Even though an accident of growth produces a new twin, the twinned orientation must present advantages if it is to grow to microscopically detectable dimensions. It is possible for the twin to have a more favourable orientation for growth into the grain being consumed, and evidence indicating that orientation may influence growth rates has been presented in an earlier section. Alternatively, the twin may permit a grain boundary configuration having a lower interfacial energy. Consider the three grain junction *ABC* shown in *Figure 28a*. The boundaries between grain *A* and grains *B* and *C* will have surface tensions σ_{AB} and σ_{AC} which depend upon the relative orientations of the grains *A*, *B* and *C*, and upon the positions of the boundaries *AB* and *AC*. Now consider the situation shown in *Figure 28b*. The boundaries between the twin *T* and the neighbouring grains will have surface tensions σ_{BT} and σ_{CT} and these values may differ from σ_{AB} and σ_{AC} .

* A twin fault has the stacking sequence *ABCBCABC*, a single error in stacking producing a twin two atom layers thick (the underlined *CB*). MATHEWSON¹⁰⁴ suggested that a structure like this could be formed by slip since the slip in the observed [110] direction in face-centred cubic metals probably results from zig-zag movements in [112] directions. An odd number of [112] displacements would produce the required stacking sequence. Heidenreich and Shockley have pointed out⁶⁶ that dislocations in face-centred cubic metals probably dissociate into half dislocations that separate, but that are connected by a stacking fault of this type. BARRETT¹⁰⁶ has presented x-ray evidence that these twin faults can be produced by deformation in silicon bearing copper.

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because the orientation of T differs from the orientation of A . In addition, there is a new boundary AT , with a surface tension σ_{AT} which numerous measurements show to be much less than the surface tension of grain boundaries. Let L_1, L_2, L_3 be the lengths of the boundaries between twin T and grains A, B and C respectively. Then if the following relationship holds:

$$L_1\sigma_{AT} + L_2\sigma_{BT} + L_3\sigma_{CT} < L_2\sigma_{AB} + L_3\sigma_{AC} \quad \dots \quad (95)$$

the total boundary energy will be decreased by introducing a twin at the grain corner. Fullman and Fisher¹⁰³ have measured the relative boundary energies in a number of cases where twins are found at boundary corners, by observing the depth of grain boundary grooves produced by thermal etching. They find that in the majority of cases the condition required by expression 95 is fulfilled. One would not

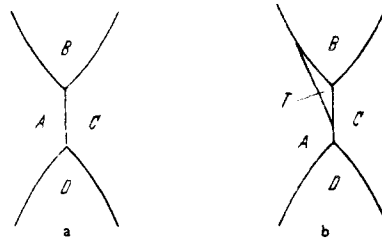


Figure 28. Twin forming in a grain corner

expect it to be fulfilled in all cases because not all twins found in grain corners will be newly formed ones. A number will be old twins which are being consumed, for these this condition need not obtain.

To summarize, annealing twins may be formed whenever a grain boundary migrates if the following conditions are fulfilled: the surface on which the twin forms must correspond to a (111) plane of the growing grain, so that a simple error in positioning of the next layer of atoms will produce a twinned orientation and the twinned orientation must be energetically or kinetically favoured. Discontinuities in the matrix being consumed favour the twinning act. Such discontinuities may be twin faults produced by deformation, or the appearance of new three grain junctions.

With this theory, most of the observations on the behaviour of annealing twins may be explained.

Absence of Twins in Cast Metals—Annealing twins are rarely if ever found in cast metals. However, grain boundary migration occurs only to a slight extent in cast metals, and in particular, the appearance of new three grain junctions is rare. Hence, there is little chance for a twinning accident to occur. Similarly, during solidification, the growing grains will encounter no discontinuities in the homogeneous melt which will be likely to induce the twinning act.

Growth of Twins during Grain Growth—The ratio of the width of twin bands to grain diameter appears to remain quite constant during grain growth. A very coarse grained metal will have grains in which the twins are many times wider than any grain that was present shortly after recrystallization. This appears to indicate that twin bands grow in width, by migration in a direction perpendicular to the (111) composition plane, during grain growth.

It has been demonstrated,⁹⁸ however, by measuring the same twin bands repeatedly during grain growth, that annealing twins do not grow in width. This is not surprising, because the low energy of the twin boundary results from the coincidence of the composition and twinning plane. An ordinary grain boundary is able to migrate past

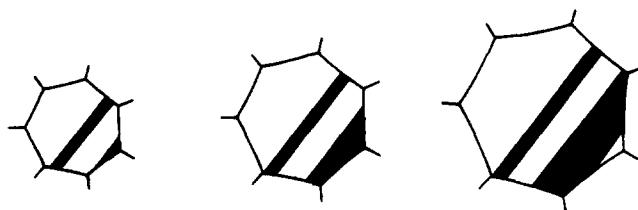


Figure 29. Mechanism for the formation of wide twins during grain growth

an inclusion because it can bend, and eventually reform on the opposite side of the inclusion while continuously decreasing its area. A coherent twin boundary is unable to do this. Since the twins do not grow in width, a mechanism is necessary to account for the appearance of wide twins in coarse grains.

One possible mechanism is shown schematically in Figure 29. A twin which forms at the corner of a grain can grow in width because one of its sides forms part of the boundary of the growing grain. It will grow in width until a second twinning act terminates it to form a complete twin band. As was indicated above, twinning probably occurs when a grain changes its number of sides. The average distance of boundary migration before a grain loses or gains a side to produce new three grain junctions will be proportional to the grain diameter, hence the average distance of boundary movement between twinning acts, and the width of newly formed twins will be proportional to grain diameter.

Mechanism for the Disappearance of Twins—The number of twins present per grain decreases rapidly in the early stages of grain growth,¹⁰⁶ and then reaches a value which appears to be quite constant for the greater part of the growth processes. Since the mechanism above indicates that twins form continuously during grain growth, both these observations indicate that twins must disappear.

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Although coherent twin boundaries, where the composition and twinning planes coincide, cannot migrate, there is evidence^{98, 101} that if a twin terminates within a grain, the non-coherent boundary can migrate, to change the size of the twinned domain. In freshly recrystallized metal, many of the twins terminate within the grain. This is probably associated with growth in a deformed matrix,

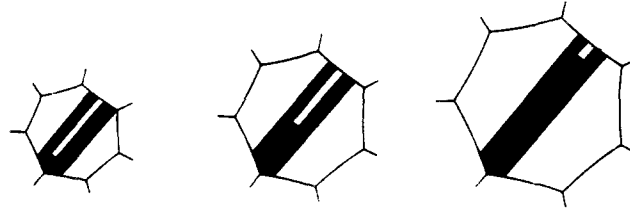


Figure 30. Migration of non-coherent twin boundary to cause disappearance of twins and increase in width of remaining ones

since both MADDIGAN and BLANK,¹⁰⁷ and BURKE and SHIAU⁶⁹ observed that grain growth in a specimen deformed too slightly to cause recrystallization, caused the appearance of many twin terminations. Apparently the residual strain energy permits the formation of the terminating interface, a phenomenon that would in most cases be impossible were surface tension the sole driving force for grain boundary migration. Once a termination is formed, the twin can decrease its length and eventually disappear, as shown in Figure 30. It should be

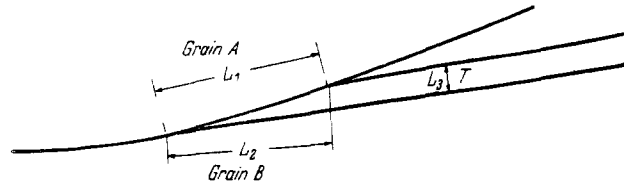


Figure 31. Conditions for the formation of non-coherent twin boundary

noted that this provides an alternate mechanism for the apparent growth in width of twins.

Fullman has further pointed out¹⁰³ that where surface energy is the sole driving force for grain growth, when a twin intersects a grain boundary with great obliquity, under certain conditions it may be energetically favourable to terminate the twin. In Figure 31 if the twin T pulls away from the grain boundary between grains A and B , then the interface along L_1 changes from AT to AB and the coherent interface L_2BT is replaced by the incoherent interface L_3BT .

Now if

$$L_1\sigma_{AT} + L_2\sigma_{BT\text{coh}} > L_1\sigma_{AB} + L_3\sigma_{BT\text{incoh}} \quad \dots \quad (96)$$

it will be energetically favourable for the twin to pull away from the boundary. The terms $\sigma_{BT\text{coh}}$ and $\sigma_{BT\text{incoh}}$ refer to the surface energies of the coherent and incoherent boundaries respectively, between grain B and its twin T . If such a termination forms the twin may eventually disappear as mentioned above.

Measurement of Interfacial Energies of Twin Boundaries

Fullman measured the interfacial energies of twin boundaries in copper and aluminium.^{100, 102} In copper the technique is interesting

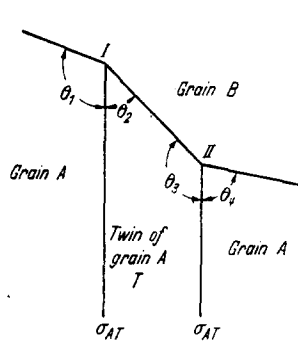


Figure 32. Angular relationships when twin intersects grain boundary

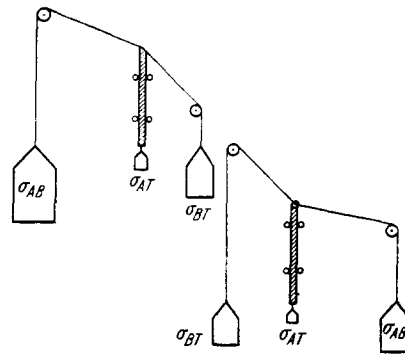


Figure 33. Mechanical analogy for Figure 32

and new. The angle opposite a twin boundary, where it intersects a grain boundary may be either greater or less than 180 degrees as shown in Figure 32.

The apparently negative surface tension of the AT boundary at the three grain junction I is a consequence of the inability of the coherent AT boundary to migrate. It can only lengthen or shorten. This is mechanically analogous to a rod, which cannot bend, and which is constrained by guides to move only longitudinally, see Figure 33. If σ_{AB} is slightly greater than σ_{BT} , then the configuration at the junctions I and II will obtain. Because of the surface tension of the twin boundaries, the left-hand part of the AB twin interface will not be quite parallel to the right-hand part of the AB interface. From the measurement of the angles θ_1 , θ_2 , θ_3 and θ_4 it is possible to determine σ_{AT} from the relationship:

$$\sigma_{AT} = \frac{\cos \theta_2 \cos \theta_4 - \cos \theta_1 \cos \theta_3}{\cos \theta_3 - \cos \theta_2} \cdot \sigma_{AB}$$

$$\text{or} \quad \sigma_{AT} = \frac{\cos \theta_2 \cos \theta_4 - \cos \theta_1 \cos \theta_3}{\cos \theta_1 - \cos \theta_4} \cdot \sigma_{BT}$$

A number of measurements made in this way indicate the surface tension of twin boundaries in copper is about 0.045 that of grain boundaries. Measurements of the same ratio, made by comparing the shape of grooves at grain boundaries and twin boundaries after annealing similar specimens in lead vapour lead to a value of 0.026, which is a reasonable check, considering the difficulty of the measurement. Thus, in copper, the twin boundary energy is from 0.03 to 0.05 that of an average grain boundary.

FULLMAN¹⁰² also measured the surface tension of the rare twin boundaries in aluminium, by measuring the angle opposite the twin boundary where it intersected the grain boundary. Actually, the surface tension of many boundaries between grains which were not accurately in twinned relationship were also made. To interpret the data, the values of the surface tension were plotted as a function of the rotation away from the precise twinned relationship. By extrapolating these data to zero rotation, a value for σ_T/σ_{AB} of 0.21 was obtained.

Variation of Intensity of Twinning from Metal to Metal—Almost any hypothesis of twinning requires that the coherent twin interface should have low energy. If this interface has a large surface tension, it will be energetically difficult to form. If the interface is formed by an accident of growth, the accident will be more improbable if a high energy interface must be formed. In particular, in terms of the conditions presented in equation 95, if σ_{AT} is large, only rarely will the left-hand side of the inequality be less than the right-hand side. Thus, twinning occurs much more frequently in copper than in aluminium because the twin boundary energy in copper is much less than in aluminium. Presumably, the minor variations in twinning intensity observed in other metals with similar histories may be explained by less important variations in the surface tension of their twin boundaries.

Alternate Theories of Twin Formation—Two important alternate theories of twin formation have been suggested. These will be considered briefly here.

MATHEWSON¹⁰⁸ has proposed that annealing twins result from the growth of mechanical twins or twin faults produced by deformation. As has been stated above, twin faults apparently do have an important role in nucleating annealing twins. However, since coherent twin boundaries cannot migrate laterally, twin faults cannot grow directly into annealing twins, nor can one account, with this hypothesis alone, for the appearance of broad twins in coarse-grained metals. Many observations require that annealing twins be formed during grain growth, in the absence of twin faults.

BURGERS¹⁰⁹ has proposed that twins in aluminium may be formed during recrystallization by stimulation. If a growing recrystallized grain meets a dislocation-bearing fragment which lies accurately in a

twinned orientation to it, the fragment may discharge its dislocations to the large grain along the common (111) plane—dislocations migrate easily in this direction. Since the fragment has discharged its dislocations, it is now stress free and able to grow at the expense of the surrounding deformed matrix. Burgers has observed a number of such grains that are thus 'stimulated' to grow, and once stimulated, grow more rapidly than the stimulating grain. His theory does not account for the more rapid growth of the stimulated grain. It is possible that this occurs because the new grain is more favourably oriented for growth into the surrounding matrix than the stimulating grain.

While the mechanism of stimulation may operate, it appears equally possible that the stimulated grain arises merely through an accident of growth of the type that has been discussed above. In any case, this hypothesis, as Burgers also suggests, is unable to account for the origin of the majority of the annealing twins found in face-centred cubic metals.

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