# ON THE POROSITY OBSERVED IN THE KIRKENDALL EFFECT*

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An attempt is made to interpret the formation of voids in the Kirkendall experiment in terms of preceding analyses of vacancy diffusion. In particular, use is made of the viewpoint that the presence of voids is related to a super-concentration of vacancies in some region of the diffusion zone. It is pointed out that the expressions obtained for the vacancy current in preceding papers permit the derivation of relations governing the superconcentration, when amplified with the introduction of appropriate concepts and parameters. It is concluded that the maximum excess concentration of vacancies is achieved in one edge of the diffusion zone when the time required for a vacancy to drift through this zone is equal to the lifetime of the vacancy and that the superconcentration of vacancies could achieve values of about 2 in the cases in which void formation has been observed, if earlier formation of voids actually does not limit the attainable supersaturation. Studies of the formation of voids in a number of couples, such as Cu-Ni, Cu-Zn, Cu-Al and Ag-Au make it possible, with suitable assumptions, to estimate the lifetime of a vacancy in this system. A value of about $10^{11}$ jumps is obtained if it is assumed that the observed voids are able to grow only when the superconcentration is near the maximum

SUR LA POROSITÉ OBSERVÉE DANS L'EFFET KIRKENDALL

Une tentative est faite, d'interpréter la formation des vides dans l'expérience de Kirkendall, en termes des analyses précédentes de la diffusion des lacunes réticulaires. Il est fait usage, plus particulièrement, du point de vue, que la présence des vides est en rapport avec la surconcentration des lacunes dans une certaine région de la zone de diffusion. Il est signalé, que les expressions obtenues pour un courant de lacunes, dans les articles précédents, permettent, quand on y introduit les concepts et paramètres appropriés, de dériver les relations qui régissent la surconcentration. Il est conclu, que l'excès maximum de la concentration est atteint dans une lisière de la zone de diffusion, quand le temps nécessaire à une lacune pour traverser cette zone est égal à la durée de vie de la lacune, et que la surconcentration de lacunes pouvait atteindre des valeurs d'environ 2 dans les cas où la formation des vides a été observée, pour autant que les vides formés antérieurement ne limitent pas la sursaturation qu'il est possible d'atteindre. Des études faites sur la formation des vides dans de nombreux couples, tels que Cu-Ni, Cu-Zn, Cu-Al et Ag-Au, permettent, en admettant certaines hypothèses, d'évaluer la durée de vie d'une lacune dans ce système. Une valeur d'environ $10^{11}$ sauts est obtenue, si on admet, que les vides observés peuvent augmenter seulement quand la surconcentration se rapproche de sa valeur maximum.

ÜBER DIE IM KIRKENDALL-EFFEKT BEOBACHTETE POROSITÄT

Es wird versucht, die Bildung von Löchern in Kirkendall-Versuchen mit Hilfe einer früher veröffentlichten Analyse der Diffusion von Leerstellen zu erklären. Dabei wird im einzelnen der Gesichtspunkt zu Grunde gelegt, dass das Vorhandensein von Löchern mit einer übergrossen Konzentration (Superkonzentration) von Leerstellen in gewissen Gebieten der Diffusionszone verknüpft ist. Es wird darauf hingewiesen, dass die Gleichungen, die in früheren Arbeiten für den Leerstellenstrom abgeleitet wurden, die Ableitung von Beziehungen, die der Superkonzentration zu Grunde liegen, gestatten, wenn die geeigneten Variablen und die notwendigen Definitionen eingeführt werden. Es ergibt sich, dass die maximale Überschusskonzentration der Leerstellen an einer Kante der Diffusionszone auftreten kann, wenn die Zeit, die eine Leerstelle braucht um durch diese Zone zu diffundieren, gleich der Lebensdauer der Leerstelle ist. Ausserdem zeigt sich, dass die Superkonzentration von Leerstellen in Fällen, in denen die Bildung von Löchern experimentell beobachtet wurde, Werte von etwa zwei erreichen könnte, falls die vorhergehende Bildung von Löchern die tatsächlich erreichbare Superkonzentration nicht begrenzt. Untersuchung der Lochbildung an einer Anzahl von Metallpaaren wie Cu-Ni, Cu-Zss, Cu-Al, und Aq-Au ermöglichen es, unter geeigneten Annahmen die Lebensdauer einer Leerstelle in diesem System abzuschätzen. Man erhält einen Wert von $10^{11}$ Platzwechseln, wenn man annimmt, dass die beobachteten Löcher nur wenn die Superkonzentration in der Nähe ihres Maximalwertes ist, wachsen können.

## 1. Introduction

The Kirkendall experiment has focussed new attention on the mechanism of diffusion in metallic systems. Since 1947, when Smigelskas and Kirkendall [1] first presented their results for diffusion in the copper-zinc system, a number of investigators, most notably Correa da Silva and Mehl [2], Alexander, Balluffi, Kuczynski and their associates at the Sylvania Electric Laboratory [3], Barnes [4], Bückle and Blin [5], and Seith and Kottman [6], have confirmed and amplified the original measurements. There is now no longer doubt that a marker shift occurs in many diffusion couples involving the face-centered cubic metals and that the factors producing this marker shift are a general feature of the mechanism of diffusion. It also seems to be generally established [3, 4] by all of the investigators that in certain couples, such as Cu-Zn, Cu-Ni, Ag-Au, porosity always develops on one side of the original interface when the Kirkendall shift occurs. Correa da Silva and Mehl suggested that the porosity might be a feature of individual couples or

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specimens. However, the work of the other investigators in the intervening period has indicated fairly conclusively that the porosity observed by Smigelskas and Kirkendall probably is a general phenomenon which must be regarded as an essential part of the diffusion process. Indeed, Barnes, who studied diffusion in the copper-nickel system, found that the volume of the pores is a substantial fraction of the volume in the Kirkendall shift. This shift would be approximately doubled in his specimens if the pores were to collapse. The present paper will be devoted to the factors which influence this porosity.

The essential historical facts concerning the theory of the Kirkendall effect are as follows:

1. Darken [7] first proposed a purely macroscopic formalism to explain the results. He suggested that each constituent atom, say $A$ and $B$, in the couple must be given its own characteristic diffusion coefficient, $D_a$ and $D_b$, with the auxiliary restriction that if an excess of atoms diffuse into or out of a given volume of the lattice, the volume would expand or contract in order to preserve the equilibrium atomic density of the alloy having composition corresponding to the constituents of the volume. This formalism leads to the Kirkendall shift whenever $D_a$ and $D_b$ differ. Still further, Darken showed that under his assumptions the chemical diffusion coefficient $D_c$ is given by the relation

$$D_c = f_b D_a + f_a D_b \tag{1}$$

where $f_a$ and $f_b$ are the atomic fractions of $A$ and $B$ atoms in the volume. Porosity plays no role in Darken's formalism, since it is assumed that the lattice will swell or shrink in such a way as to maintain the equilibrium density.

2. The writer [8] made a first attempt at an atomic interpretation of the Kirkendall effect using vacancy theory and the assumption that a given vacancy would have different probabilities of interchanging places with an $A$ atom and with a $B$ atom. This theoretical treatment, which contained very general assumptions and which was initiated in order to shed light on Johnson's experiments [9] concerning the chemical and radioactive diffusion coefficients in the silver-gold system, treated the variable which describes vacancy density in the system as a disposable function to be determined by separate reasoning. The writer focussed attention on the special case in which the vacancy current $I_v$ is constant in space throughout the diffusion zone and varies with time as $1/\sqrt{t}$, as if this current arose from the diffusion of vacancies between two reservoirs whose dimensions are large compared to the dimensions of the diffusion zone. This assumption concerning the vacancy current does not lead to Darken's equations, although it did give a qualitative interpretation of the knowledge concerning the Kirkendall effect which existed at the time.

3. Bardeen [10] then demonstrated that Darken's equations can be derived with the use of vacancy theory if one assumes that there is a sufficient density of sources and sinks of vacancies throughout the diffusion zone to maintain the equilibrium concentration of vacancies over regions small compared with the dimensions of the diffusion zone. This analysis was based on the use of a very simple model of the diffusing system.

4. The writer [11] subsequently showed, first, that his general equations contain Bardeen's solution as a special case of a family of solutions obtained when the density of vacancies has the equilibrium value at each position, and, second, that Darken's equations also follow if diffusion occurs by the interstitial mechanism. In fact, there is a very close parallel between the equations derived from vacancy and interstitial diffusion. Thus, as intuition indicates, the validity of Darken's equations does not allow one to distinguish between interstitial and vacancy diffusion.

5. Bardeen and Herring [12] summarized the existing situation in a review article prepared in the fall of 1950. They placed emphasis upon the hope, gained from available experiments, that one might expect to have the vacancy distribution at equilibrium in most typical systems, so that the behavior of a diffusion couple would generally be amenable to the regularities implied in Darken's equations. They stressed the fact that this would require that the lifetime of vacancies be limited, and placed an upper limit of $10^9$ jumps as the desired maximum for practical obedience to Darken's relation. They felt, in turn, that this was a feasible upper limit in view of the fact that of the order of one atom in $10^7$ is believed to be near the center of a dislocation line in typical materials. The apparently universal appearance of porosity whenever the Kirkendall effect is strong compels us to re-examine the basis of this viewpoint.

It is natural to suppose that the pitting observed during diffusion arises as the result of a large deviation from the equilibrium density of imperfections—a superconcentration of vacancies or a subnormal concentration of interstitial atoms. Presumably the ideal sources for vacant lattice sites or interstitial atoms within single crystals are jogs on long dislocations with edge components. These can act as

sources or sinks with the equilibrium energy. Such sites, along with grain boundaries in polycrystalline specimens, will act as sinks for vacancies or sources for interstitial atoms even when there are small deviations from the equilibrium concentrations. Naturally they may also act when the deviations from equilibrium are large. There is no good reason why voids should form when long edge dislocations act as sinks for vacancies or sources for interstitial atoms if the density is very close to equilibrium since the consequent "climbing" of dislocations should be compensated by continuous contraction of the specimen.

Small voids, cracks, or inclusions may act as sinks for vacancies or sources for interstitial atoms, and produce large voids when an appropriate supersaturation of the former or subnormal concentration of the latter is present. In the simple case in which the initial voids are spheres of radius $r$, the excess concentration of vacancies, $N_v$, needed to make them grow is given by the Thomson-Gibbs relation [13]

$$\ln \frac{N_v}{N_{vo}} = \frac{2s}{kTNr}$$

where $N_{vo}$ is the equilibrium value of the vacancy density, $s$ is the surface energy per unit area, $k$ is Boltzmann's constant, $T$ is the absolute temperature, and $N$ is the atomic density. The nuclei of these voids may be occupied with foreign material and hence preserved under equilibrium conditions. In typical cases, vacancies will condense at spherical voids containing the volume equivalent to about 1,000 vacant lattice sites if $N_v/N_{vo}$ is in the vicinity of 2, or greater.

Vacancies may condense to form voids in the perfect crystal if $N_v/N_{vo}$ is of the order of 100, or greater. In the case of the interstitial mechanism, voids may be produced in the perfect lattice by the generation of interstitial atoms if the density of interstitials is at least 100 times below normal.

When $N_v/N_{vo}$ is very near to unity, the Thompson-Gibbs relation may be written

$$R \cong \frac{2s}{kTNr} \qquad (R \ll 1)$$

where $R = (N_v/N_{vo}) - 1$ is the *relative excess concentration*.

At the present time we do not know enough about the nuclei on which the voids form to give effective values of $r$ that may be associated with them. Or, expressed in another way, we do not know the critical value $R_c$ of the relative excess concentration $R$ needed to cause these nuclei to accumulate vacancies and grow into pores. Evidence bearing on this point will be discussed in Section IV. In general it appears that the effective value of $r$ may vary from one specimen to another, depending upon the history of the specimen, as well as from one nucleus to another in the same specimen. That is, there appears to be considerable heterogeneity in the nuclei responsible for pores in the various substances in which porosity has been observed to date. It will be demonstrated, in the next section, that values of the excess relative concentration $R$ in the neighborhood of unity are possible in typical materials showing the Kirkendall shift, at an appropriate phase in the diffusion cycle. Since this possibility exists, particular attention will be devoted to the case in which values of $R$ of the order of unity are necessary to form pores. This would be the case if the nuclei were homogeneous and if the largest radius of curvature of the nuclei was of the order of 10 atomic diameters. Thus if they were spheres they would be small even on the scale of the electron microscope. The specimens of Cu-Ni investigated by Barnes may actually correspond to this limiting state of affairs. Herring [private communication] has stressed the point of view that the nuclei responsible for the porosity observed in connection with the Kirkendall effect in many materials may operate for values of $R$ much smaller than unity, of the order of 1 per cent or even less. This is equivalent to assuming that the corresponding effective values of $r$ are of the order of 1,000 atomic distances, or possibly larger. There is evidence, discussed at least partly in Section IV, to support this point of view. What is most likely is that there is a distribution in range of the effective values of $r$ and that at least a portion of the pores observed form on nuclei for which $r$ is in the vicinity of 1,000 atomic distances. On the other hand it is by no means certain that such nuclei are dominant in all materials. The issue must apparently be settled by further experiment. Unfortunately it is not a trivial one, for, as we shall see, the following analysis makes it possible to obtain estimates of the mean number of jumps vacancies make between source and sink, provided one assumes values of the excess concentration needed to condense vacancies. The results are sensitive to the value of $R_c$ that is assumed necessary in order to generate pores.

## II. Formal Concepts

For simplicity, we shall assume that diffusion occurs primarily by the vacancy process. The known

experimental facts do not seem to permit a distinction between the vacancy and interstitial mechanisms at the present time; however, the theoretical analyses make the former seem much more likely. In addition, the qualitative consequences apparently would be identical in the two cases as far as matters of interest in the present discussion are concerned.

The writer [9, 11] has shown that a formal approach to the discussion of vacancy diffusion can be made by introduction of the quantities $\pi_a(n_1, n_2)$ and $\pi_b(n_1, n_2)$ which represent the probabilities per unit time that a vacancy in one plane normal to the concentration gradient, in which the planar density of $A$ atoms is $n_1$, will jump to the next parallel plane, in which the planar density of $A$ atoms is $n_2$, in such a way as to interchange places with the $A$ and $B$ atom, respectively. $\pi(n_1, n_2) = \pi_a(n_1, n_2) + \pi_b(n_1, n_2)$ is the total probability for the jump between planes 1 and 2. In terms of these quantities the vacancy current is $I_v$

$$(2)\quad I_v = -\pi(n_a)\lambda\frac{dn_v}{dx} + n_v\left(-\frac{\partial\pi}{\partial\xi} + \frac{\partial\pi}{\partial\eta}\right)\lambda\frac{dn_a}{dx}$$

in which $\lambda$ is the interplanar spacing, $n_a$ and $n_v$ are the average planar densities of $A$ atoms and vacancies in a given vicinity, $\pi(n_a)$ is the value of $\pi(n_1, n_2)$ when $n_1 = n_2 = n_a$, and $\partial\pi/\partial\xi$ and $\partial\pi/\partial\eta$ are the derivatives of $\pi(n_1, n_2)$ with respect to $n_1$ and $n_2$ evaluated for $n_1 = n_2 = n_a$. It is assumed the concentration gradient is in the $x$ direction. In the following it will be convenient to replace the mean planar densities $n_i$ by the mean volume densities $N_i$ in accordance with the relation

$$(3)\quad N_i = n_i/\lambda.$$

Similarly, as a convenient shorthand, we shall write

$$(4)\quad \left(\frac{\partial\pi}{\partial N}\right) \equiv \lambda\left(-\frac{\partial\pi}{\partial\xi} + \frac{\partial\pi}{\partial\eta}\right).$$

Equation (2) then becomes

$$(5)\quad I_v = -\pi\lambda^2\frac{dN_v}{dx} + N_v\left(\frac{\partial\pi}{\partial N}\right)\lambda^2\frac{dN_a}{dx}.$$

The first term in (5) evidently represents the normal Fick term for the vacancy current associated with the vacancy gradient $dN_v/dx$, the diffusion coefficient being

$$(6)\quad D_v = \pi\lambda^2.$$

The second term is the Kirkendall term, for it vanishes when the chemical gradient is absent and evidently, describes the ability of the chemical gradient to "pump" vacancies from one portion of the lattice to another. The critical parameter in the Kirkendall term clearly is the quantity (4) for it provides a measure of the anisotropy of the lattice, as far as vacancies are concerned, in a region where a chemical gradient exists. The coefficient of $N_v$ in the second term of (5) namely

$$(7)\quad v = \left(\frac{\partial\pi}{\partial N}\right)\lambda^2\frac{dN_a}{dx}$$

is the average velocity with which the vacancy is pumped through the gradient.

It is interesting, for the purposes of the following discussion, to consider the case in which $\pi(n_1, n_2)$ has the simple form

$$(8)\quad \pi(n_1, n_2) = \alpha n_2^{\rho}$$

in which $\alpha$ and $\rho$ are constants. This expression leads to the simple relation

$$(9)\quad N_a\left(\frac{\partial\pi}{\partial N}\right) = \rho\pi(N_a)$$

so that the parameter $\rho$ provides a somewhat primitive measure of what might be termed the "order" of the Kirkendall effect. The form (8) has more merit than mere mathematical convenience. For example, the case $\rho = 0$ corresponds to the situation in which $A$ and $B$ atoms are identical as far as vacancy migration is concerned. It describes the circumstance in which the jump frequency $\pi$ is independent of the relative density of $A$ and $B$ atoms in the neighboring planes. Similarly the case $\rho = 1$ represents a situation in which the vacancies strongly prefer to exchange places with $A$ atoms and in which the $B$ atoms merely dilute the $A$ atoms. Finally, the case in which $\rho > 1$ corresponds to a simplified form of the situation in which the vacancies prefer to interchange with $A$ atoms and in which the presence of $B$ atoms has an inhibiting influence upon the rate of interchange of a given vacancy with an $A$ atom in the neighboring plane. Clearly the cases in which $\rho \neq 0$ correspond only schematically to real ones; however they will provide valuable insight in the following. The use of (8) without an added constant term implies that when $\rho \neq 0$ the jump frequency is negligible in the specimen of pure $B$ atoms. This is probably not invariably the case in actual specimens, but is frequently true. For example, it is probably true in CuNi at 1080°C.

It is clear that if $N_v$ maintains the equilibrium value corresponding to the local concentration in each region of the specimen, $I_v$ in (5) will be purely a function of composition. This is one of the condi-

tions on the vacancy diffusion mechanism which is requisite if Darken's equations are to be valid.

In addition to the previous, essentially exact formal relations (2) to (7), it is convenient to introduce the following more approximate, or average relationships:

1. For simplicity, we shall assume that the chemical gradient extends uniformly over the region

$$d = 2\sqrt{(D_c t)} \tag{10}$$

in which $D_c$ is the average chemical diffusion coefficient (see Equation (1)) and $t$ is the time since initiation of the diffusion experiment with plane parallel slabs. Actually, the chemical gradient will be more nearly like a Gaussian function; however, the introduction of the parameter $d$ provides a useful simplification.

In the approximation in which the concentration gradient is treated as uniform over the distance $d$, the gradient is

$$\frac{dN_a}{dx} = \frac{\Delta N_a}{d} \tag{11}$$

where $\Delta N_a$ is the difference in concentration across the entire couple.

2. We shall assume that the sources and sinks for vacancies are distributed throughout the single crystals of which the specimens are composed. Experimental evidence shows that grain boundaries frequently are excellent sources and sinks; however, attention will be focussed on the sources and sinks within the grains which persumably are closely associated with dislocations when the density of vacancies is near to the equilibrium value. If $N_t$ is the density of sinks which may presumably also act as sources and $\sigma_t$ is the eross section for capture of a wandering vacancy by a sink, the number of jumps a free vacancy makes on the average before being captured is

$$\omega = \frac{1}{N_t \sigma_t \lambda} \tag{12}$$

and the mean time the vacancy is free is

$$T = \frac{1}{\nu N_t \sigma_t \lambda} \tag{13}$$

where $\nu$ is the jump frequency, which differs from $\pi(n_a)$ by a constant near unity and may be set equal to this quantity in a semi-quantitative treatment. Among other things, $T$ is the critical relaxation time for establishing the equilibrium density of vacancies in the normal crystal.

3. The average distance $\Delta$ which a vacancy may drift in the concentration gradient $dN_a/dx$ under the pumping action of the gradient before being captured at a sink is given by the relation

$$\Delta = vT = \left(\frac{\partial \pi}{\partial N}\right) \lambda^2 \frac{dN_a}{dx} \frac{1}{\nu N_t \sigma_t \lambda} . \tag{14}$$

In the approximation in which $dN_a/dx$ is replaced by (11), $\nu$ is replaced by $\pi(n_a)$, and the latter is assumed to satisfy the relation (9), (14) becomes

$$\Delta = \rho \frac{\Delta N_a}{N_a} \frac{\lambda}{N_t \sigma_t d} = \rho \frac{\Delta N_a}{N_a} \frac{\lambda^2}{d} \omega . \tag{15}$$

As a distance, $\Delta$ has direct physical meaning only when it is smaller than or comparable to $d$. In other cases the calculated value is an important physical parameter of the theory.

4. Consider a group of vacancies which initially are closely spaced and are allowed to migrate in the concentration gradient. Although they migrate with the average velocity (7), they will tend to become dispersed as a result of Brownian motion. We shall have use for the amount of dispersion in travelling distance $d$ and in travelling for a time $T$.

The mean time for a vacancy to drift a distance $d$ is

$$t_d = \frac{d}{v} . \tag{16}$$

The dispersion distance during this time may be expressed by the quantity

$$\begin{aligned} \delta d &= 2\sqrt{D_v t_d} = 2\left[\frac{\pi(n_a) d}{\left(\frac{\partial \pi}{\partial N}\right)\frac{dN_a}{dx}}\right]^{\frac{1}{2}} \\ &\cong 2d\left(\frac{N_a}{\rho \Delta N_a}\right)^{\frac{1}{2}} . \end{aligned} \tag{17}$$

The right-hand expression is valid when the approximations (9) and (11) are used. In this simplified limit, the fractional dispersion $\delta d/d$ has the value $2\sqrt{(N_a/\rho \Delta N_a)}$, which is independent of $d$ and hence of time.

The corresponding dispresion distance $\delta\Delta$ for time $T$ is $2\sqrt{(D_v T)}$ which, using (15), can be expressed in the form

$$\delta\Delta = \delta d\left(\frac{\Delta}{d}\right)^{\frac{1}{2}} = 2\lambda\omega^{\frac{1}{2}} . \tag{18}$$

The quantity $\delta d/d$ will be of considerable interest in the next section. It evidently can be small compared with unity only if $\rho$ is larger than unity and if $N_a/\Delta N_a$ is not too great compared with unity.

It is interesting and useful to estimate the value

of $\rho$ which obtains in the cases in which the Kirkendall effect has been measured and is known to be large (for example, the case of 73Cu27Zn for which $D_{Zn}/D_{Cu} \backsim 5.8$). According to Equation (23) of reference [11] the velocity $V$ of displacement of a given segment of the diffusion zone at which the concentration gradient is $dN_a/dx$ is

$$V = \frac{1}{N} I_v$$

in which $N$ is the total density of atoms (designated by $c$ in reference [11]), provided the vacancies condense, as is assumed to be the case in the ideal Kirkendall experiment. The experiments carried out thus far correspond to cases in which the vacancies usually migrate to the member of the couple having the constituent with highest vapor pressure (for example Zn in Cu-CuZn and Cu in Cu-Ni). This is also the member in which one should expect the higher density of vacancies at any given temperature. Thus the main vacancy flow in these specimens is opposite to that given by the first term in (5), and we may conclude that the second term gives a greater contribution.

If we assume we are dealing with the limit in which $N_v$ is determined by the concentration of $A$ atoms, so that near the interface

$$\frac{dN_v}{dx} = \frac{dN_v}{dN_a}\frac{dN_a}{dx} \sim \frac{N_v}{\Delta N_a}\frac{dN_a}{dx},$$

the ratio of the absolute value of the second term in (5) to the first is, in order of magnitude,

$$\rho \frac{\Delta N_a}{N_a}.$$

Thus $\rho$ should not be small compared with unity.

Further evidence in the same direction is obtained by comparing $Vt$, the Kirkendall shift in time $t$, with $d$, the diffusion range, given by (10). We readily find, using the relation (11),

$$\frac{Vt}{d} \sim \rho \frac{\Delta N_a}{N_a}\frac{N_v}{N}\frac{D_v}{D_c}.$$

Since $D_v/D_c$ should be of the order of $N/N_v$ whenever the Johnson-Wagner effect is not prominent, it follows that $\rho\, \Delta N_a/N_a$ should not be small compared with unity if the Kirkendall effect is appreciable.

## III. The Migration of Vacancies in the Diffusion Zone

In the standard diffusion couple, $d$ is initially zero and increases linearly with the square root of the time (Equation (10)). On the other hand, $\Delta$ is initially very large, as a parameter at least, and decreases inversely as the square root of the time in the approximation (15). If diffusion continues sufficiently, $d$ and $\Delta$ will cross and their relative values will be reversed. The limit in which $\Delta$ is small compared with $d$, that is, the limit of long time, evidently corresponds to the case in which the local density of vacancies is maintained very close to the equilibrium value, for a given vacancy travels only a relatively short distance along the chemical gradient in passing from the source to the sink. In brief, the situation in which $\Delta$ is small compared with $d$ corresponds closely to the approximation described by Bardeen [10] and emphasized by Bardeen and Herring [12], which leads to Darken's equations; the drift current does not upset radically the local equilibrium of vacancies.

The opposite approximation, in which $\Delta$ is larger than or comparable to $d$, is the one in which we may expect to find the conditions which lead to vacancy concentrations appreciably different from the equilibrium concentration. For then the vacancies produced in the diffusion zone may drift to one end of this zone and accumulate there so as to give an abnormally high concentration.

Assume for the moment that the rate of vacancy production per unit volume per unit time in the diffusion zone is q. Since the relaxation time for the attainment of equilibrium is $T$ (Equation (13)), the equilibrium density of vacancies is assumed to be $qT$. The number of vacancies generated in time $t$ in a volume of the gradient domain possessing a thickness $d$ parallel to the gradient and unit cross section in the normal direction is $dqt$. These vacancies will be swept to the edge of the diffusion zone by the gradient and will be compressed to a thickness $2\sqrt{(D_v t)}$ if, as we shall assume to be the case, the principal factor limiting compression is Brownian motion. Thus the concentration of the displaced vacancies in this compressed zone which are collected in time $t$, assumed small compared with $T$, is

$$\frac{dqt}{2\sqrt{(D_v t)}} \qquad (t < T) \tag{19}$$

or the density $R_t$ relative to the equilibrium value $qT$ is

$$R_t = \frac{dqt}{2\sqrt{(D_v t)}}\frac{1}{qT} = \frac{d}{\delta\Delta}\left(\frac{t}{T}\right)^{\frac{1}{2}} \quad (t < T, \Delta > d) \tag{20}$$

Before employing (20), we must decide whether the displaced vacancies which reach the edge of the diffusion zone constitute the entire concentration there or whether they add to an appreciable density

of vacancies already present which have not been swept away because the gradient in concentration is not sufficiently high. In the first case, $R_t$ would give the relative concentration in the end zone, whereas in the extreme instance of the second case, the relative density in this zone would be $1 + R_t$. This issue could be determined precisely on theoretical grounds only by solving the basic equations governing vacancy migration, generation, and disappearance for a number of typical cases and examining the results. A somewhat simplified form of this procedure, which is analogous to that employed in solving the equations governing the distribution of neutrons in nuclear reactors [14], is developed in the appendix to this paper and is solved for a typical case. The results bear out the conclusions drawn on qualitative grounds in the next paragraphs. It is evident, however, that the more mathematical approach could be expanded with profit.

If $R_t$ is large compared with unity for a substantial part of the range of time of interest, namely when $t \leqslant T$, the isssue is not critical since an appreciable supersaturation of vacancies is guaranteed. On the other hand, when $R_t$ is near to or smaller than unity throughout the range of time, we must conclude that the random notion of the vacancies is sufficiently great that the bunching which results from the gradient is comparatively weak even in the region where the gradient is strongest. It follows that the influence of the gradient should be even less in the end zone where the vacancies tend to accumulate; hence the vacancies generated in that region should be added to those which arrive there by displacement. In brief, it seems appropriate to assume that the effective concentration of vacancies in the end zone is $1 + R_t$, so that $R_t$ measures the relative concentration *above* saturation. Since $R_t$ is always positive, we may expect a slight degree of supersaturation under all conditions, even though this may be insufficient to produce pores.

In the opposite limit in which $\Delta$ is small compared with $d$, only a fraction of the vacancies produced in the diffusion zone accumulate at the boundary of this zone since most die while migrating in the direction of the boundary. The value $R$ of the excess relative concentration may be determined easily by the condition that the vacancy current in the diffusion zone arising from the drift velocity (7), namely $\rho N_{vo} D_v \Delta N_a / N_a d$, where $N_{vo}$ is the equilibrium density of vacancies, be equal to the diffusion current in the region beyond the boundary where there is no concentration gradient. Since the relaxation distance in the latter region is $\delta\Delta$, the second current is $D_v \delta N_v / \delta\Delta$, where $\delta N_v$ is the excess concentration of vacancies at the boundary. We obtain from this relation

$$R \sim \rho \frac{\Delta N_a}{N_a} \frac{\delta\Delta}{d} = 2\rho \frac{\Delta N_a}{N_a} \frac{\lambda}{d} \omega^{\frac{1}{2}}. \tag{21}$$

This corresponds to case (b) in the Appendix.

The condition necessary for strong supersaturation during the diffusion process is that $R_t$ (Equation (20)) be comparable to or greater than unity when (20) takes its maximum value for $t = T$, that is

$$R_T = \frac{d}{\delta\Delta} \geqslant 1$$

or

$$R_T = \frac{d}{\delta d} \left(\frac{d}{\Delta}\right)^{\frac{1}{2}} \geqslant 1 \qquad (\Delta > d) \tag{22}$$

(see Equation (18)).

In the approximation corresponding to the right-hand side of (17), the ratio $d/\delta d$ is independent of $d$ or $t$, that is, is a constant of the diffusing system. Hence (22) will be satisfied at some time during the diffusion process if

$$\frac{d}{\delta d} > 1.$$

The left-hand side of the relation (22) shows that under all conditions the time at which the greatest supersaturation of vacancies occurs is that for which $\Delta$ and $d$ are about equal.

Conversely, we saw at the end of the last section that we have good reason to expect $\rho\Delta N_a/N_a$, and hence $d/\delta d$, to be near unity for couples having a strong Kirkendall effect. It follows that in such systems $R_T$ should be near unity when $\Delta$ and $d$ become equal. Since $\Delta$ involves the unknown $N_v\sigma_v$, or $T$, we cannot determine directly, at least at present, the value of $d$ at which this occurs. Instead we must attempt to infer the result from experiments with use of what at present are somewhat arbitrary hypotheses.

It is natural, as remarked in Section I, to assume that the ease with which pores are formed is directly related to the degree of supersaturation. We shall assume at start that they will first occur at irregular sites, such as voids and small inclusions, when the concentration of vacancies is of the order of twice the equilibrium concentration in moderately perfect single crystals. This will not happen during the initial phase of diffusion, in what we have termed the ideal case, for $R_t$ should approach zero at values of $t$ small compared with $T$, according to Equation (20).

In actual systems, it is possible that $T$ is relatively small near the junction of the couple because of a relatively high degree of imperfection at the interface. Thus pores might form there even though they would not if $T$ had the average value for the remainder of the specimen. Similarly, once pores are formed in a given region of the specimen, because of a suitable excess concentration of vacancies, the pores may act as new sources and sinks for vacancies and decrease $T$ locally. The jogs on incompleted rows of atoms on incomplete surfaces should act as effectively as jogs on dislocation lines in producing and absorbing vacancies.

Thus $T$ may actually be variable during the course of the diffusion cycle, being large until porosity develops in such a way that the spacing between pores is smaller than the value of $\delta\Delta$ which obtained prior to the formation of pores. It is even possible in particular cases that the lifetime of vacancies is determined by the geometry of the specimens. This will occur if the linear dimensions of the specimen are not large compared with $\delta\Delta$ determined from the volume density of trapping centers, so that the vacancies have an appreciable chance of dying at the surface.

As $d$ increases, the pores formed during the early portion of diffusion may find themselves in a region of sub-equilibrium concentration of vacancies because the boundaries of the diffusion zone have continued to move and all vacancies are swept on to the new boundary. Under these conditions the old pores may act primarily as sources of vacancies and decrease in size, the vacancies being reabsorbed at the diffusion boundary.

In any event, new pores should cease being formed when $d$ exceeds $\Delta$ sufficiently. The critical value of $d$ for which this occurs depends upon $R_c$, the critical value of the excess relative concentration needed to form pores about the available nuclei. If $R_c$ is near unity, pore formation should cease when $d$ exceeds $\Delta$ appreciably, or, using (15), when

$$d \sim \left(\rho \frac{\Delta N_a}{N_a}\omega\right)^{\frac{1}{2}} \lambda \sim \omega^{\frac{1}{2}}\lambda, \tag{23a}$$

the right-hand approximation being valid when $\rho\Delta N_a/N_a \backsim 1$. On the other hand, if $R_c$ is much smaller than unity, pore formation will cease when $d$ increases to the point where $R$ given by (21) decreases to the value $R_c$. This is equivalent to the conditions, analogous to (23a),

$$d \sim 2\rho \frac{\Delta N_a}{N_a}\omega^{\frac{1}{2}}\frac{\lambda}{R_c} \sim \omega^{\frac{1}{2}}\frac{\lambda}{R_c}. \tag{23b}$$

As was remarked at the end of the previous section, we do not have at present exact values of $R_c$. Indeed there is evidence (Section IV) to show that $R_c$ may vary from specimen to specimen and from one region to another within a given specimen. It is convenient for present purposes to focus some attention on the case in which the nuclei are fairly homogeneous and in which $R_c$ is of the order of unity, examining the consequences of these assumptions. Under such conditions the relations (23a) should be used. We shall postulate that the width of the porous zone is equal to the value of $d$ for which (23a) is valid. This postulate will allow us to determine values of $N_t\sigma_t$, or of $\omega$, typical of the zone *when pores are present*. These values of $N_t$ presumably are larger than those which obtain for a non-porous specimen since the surfaces of the relatively large pores provide traps which can act even if the excess concentration is small.

If $R_c$ actually is much smaller than unity, of the order of $10^{-2}$ or less, the relations (23b) would be more appropriate to use instead. It is evident that the values of $\omega$ that would be computed in the two cases from the same values of $d$ would differ in the ratio $R_c^2$ and hence could be radically different.

The specimens of Cu-Ni studied by Barnes seem to provide ideal examples for this type of analysis. He has found that when measurements are carried out at sufficiently high temperature (1010°C to 1080°C), the pores which form in a late stage of the diffusion cycle tend to be large and to cluster in a plane normal to the diffusion gradient, that is, parallel to the original interface, as if any pores which might have formed initially near the interface were dissolved. In this connection Barnes has noted that the volume density of pores in his specimens is approximately constant, independent of time and temperature for which diffusion occurred. This, in turn, suggests that in his specimens at least the nuclei responsible for pore formation may be very homogeneous. In a typical case, illustrated by Figures 5 and 6 of his manuscript, the pores are about 5 mm from the original boundary on a scale of magnification of 150, corresponding to $\Delta = 7 \times 10^{-3}$ cm if the condition (23a) is valid. The corresponding value of $N_t\sigma_t$ derived from Equation (23a) by setting $\Delta N_a/N_a = 1$ and $\lambda = 2 \times 10^{-8}$ cm is $4 \times 10^{-4}\rho$ cm$^{-1}$. If we assume that at these temperatures the vacancy must be captured directly by a jog at a dislocation or on a surface of a pore to be retained and that, as a result, $\sigma_t \backsim 10^{-15}$ cm$^2$, we obtain

$$N_t \backsim 4 \times 10^{11}\,\rho \text{ cm}^{-3}.$$

Apparently it is necessary to assume that $\rho$ is at least of the order of unity in order to obtain consistent results in the cases in which pronounced Kirkendall effect is observed. In any case, we conclude that $N_t$ is of the order of $10^{12}$ cm$^{-3}$ if $R_c \backsim 1$. Since the density of atomic sites which are immediately adjacent to edge dislocation lines should be nearer to $10^{15}$ cm$^{-3}$ in typical materials, if the customary estimate that there are about $10^8$ dislocation lines per cm$^2$ is correct, this value of $N_t$ is in accordance with the notion that only a small fraction ($\backsim 10^{-3}$) of the places along dislocation lines can act as sources or sinks for vacancies at the temperature at which the measurements are made.

Balluffi and Alexander [3] have made somewhat similar observations on the copper-nickel system in specimens held at 1055°C for 239 hours, and have found porosity extending over a distance about three times larger than that observed in Barnes's specimens (see Fig. 7 in the second paper of reference [3]). If we make the somewhat dubious assumption that $R_c$ is the same in the two cases, we apparently must conclude that $N_t\sigma_t/\rho$ is about ten times smaller in the specimens studied by Balluffi and Alexander than in those examined by Barnes, for $N_t\sigma_t/\rho$ varies inversely as the square of the thickness of this zone (see Equation (23a) or Equation (15) for the case in which $\Delta = d$). Since there is no reason to expect $\rho$ to be different in the two cases, we may then conclude that $N_t\sigma_t$ is ten times smaller in the first case.

Smigelskas and Kirkendall seem to have observed pitting in 70-30 brass specimens, studied at 785°C, at distances at least ten times larger than those observed in Cu-Ni by Barnes. Similar results are found by Balluffi and Alexander [3] at 880°C. If the condition $R_c \backsim 1$ is valid, we apparently must conclude that $N_t\sigma_t/\rho$ is at least thirty times smaller in typical specimens of this material than in the specimens of Cu-Ni, at the temperature of measurement, for $N_t\sigma_t/\rho$ varies inversely as the square of the thickness of this zone and only directly as the first power of $\Delta N_a/N_a$. It is difficult to indicate the source of this difference, inasmuch as at least three variables are involved. At the present time, it seems reasonable to assume tentatively that a value of $\rho$ larger than 5 is excessive and conclude that $N_t\sigma_t$ is at least ten times smaller in brass than in CuNi.

The ratio $d/\delta d$ has a value of about 0.6 for the brass specimens if $\rho$ is assumed to be about 5. This is sufficiently near unity to suggest no conflict with the view that the degree of supersaturation required to produce voids corresponds to $R_T \backsim 1$ or greater.

Bückle and Blin [5] have observed voids at a distance of $3 \times 10^{-2}$ cm from the interface in specimens of copper interdiffusing with 7 per cent Cu-Al alloy for 25 days at 800°C. Thus $N_t\sigma_t/\rho$ seems to be of the order of one hundred times smaller in this case than in that of Cu-Ni if $R_c$ is the same. Again it would appear reasonable to suppose that $N_t\sigma_t$ is substantially smaller in this couple than in Cu-Ni.

Finally, Balluffi and Alexander [3] have observed porosity over a distance of about $1.2 \times 10^{-2}$ cm in couples of silver and gold held at 920°C for 44 hours. In this example $N_t\sigma_t/\rho$ appears to be about one-fourth as large as in Barnes's specimens of Cu-Ni, if $R_c$ is the same in the two cases.

## IV. Concluding Comments

Although the preceding discussion seems to tie pore formation into the general picture of events surrounding the Kirkendall effect, it leaves many basic questions either unanswered or in little more than a qualitative state. For example, several key issues are as follows:

1. What are the nuclei of the voids? Several investigators have speculated on this point. They could be a configuration of dislocations, such as the spiral prismatic dislocation [15], which is unable to achieve equilibrium when in a highly supersaturated atmosphere of vacancies and forms a void as a result of the rapid accumulation. They could also be small voids or inclusions (motes) about which a superconcentration of vacancies condense. Or, the voids could form in the perfect lattice when the superconcentration is high. The first and second processes are not radically different; however, it would be interesting to know if the third process actually occurs. The writer is inclined to discount it since it requires values of $R_T \backsim 100$ and hence values of $\rho$ of the order of $10^4$, which seem exceedingly high. Granting this, we are left with the outstanding problem of determining the excess relative concentration $R_c$ needed to cause the effective nuclei to form voids.

2. It is not entirely clear why porosity varies so much from one specimen of a given material to another or why it is so much more broadly distributed throughout the diffusion zone in the brass specimens that have been studied than in Cu-Ni or Ag-Au. Barnes has suggested that the pores tend to become large and localized at high temperatures. There is little doubt that this is true of the Cu-Ni specimens he studied in the range between 1010°C and 1080°C, just below the melting point of Cu. On the other hand Balluffi and Alexander seem to

have observed broadly distributed porosity both in couples of copper and nickel, in the same temperature range, and in couples of copper and brass which were treated at 880°C, which is close to the melting point of the 70-30 brass used, namely 902°C. From the published figures, the writer cannot detect a significant difference between the distribution of pores in these specimens of brass and those observed by Smigelskas and Kirkendall at 785°C; however the pores may be larger in the first case.

The most reasonable explanation of the variation in porosity between specimens is that there may be a distinct difference in the size of the nuclei for pores in different specimens, both of like and unlike materials. It has been assumed implicitly in the previous sections that the nuclei for pores are more or less the same in various cases, having a fairly well defined equilibrium vapor pressure for vacancies. Actually the nuclei may vary over a wide range from one material to another. In fact it is not unreasonable to suppose that there may be a range of nuclei within a given specimen. In the couples studied at the Sylvania Laboratories, one frequently observes a few pores relatively far from the principal group adjacent to the fiducial markers, as if the distribution of nuclei were so wide that a relatively few nuclei could act to form pores for excess concentration of an order of magnitude less than the average.

This aspect of the present topic might be greatly clarified by observations on couples in which one or both specimens contain, as a result of intentional addition, specified amounts of fine sols of materials of known size which are not soluble in the metals. For example silica sols or fine carbon blacks in the range of 50Å or less might be ideal for this purpose.

It seems difficult to draw further reliable conclusions concerning the pores from the available experimental information, although a few tentative suggestions can be gleaned, particularly from Barnes's measurements. He has found in the case of the Cu-Ni specimens that the typical couple swells in such a way that the expansion varies as $\sqrt{t}$, at least during the initial period of about 25 hours when the diffusion takes place at 1065°C. This behavior was studied over a range of time extending from about 15 minutes to somewhat more than 25 hours in two specimens. The diffusion distance $d$ is of the order of $10^{-4}$ cm at the time of the first observations. This result suggests that pores form very early in the diffusion process and behave in a "uniform" manner during the subsequent history of the specimen, if we assume that the swelling is a result of the growth of pores. Were it certain that $\omega$ is as small as $10^8$ or $10^9$, so that the Darken-Bardeen approximation would be valid for values of $d$ of the order of $10^{-4}$ cm and larger, we might conclude that a fixed fraction of the vacancy current, which would vary as $1/\sqrt{t}$ under these conditions, goes into the formation of pores. It is difficult to believe that any such simple conclusion can be drawn in a direct manner, however, for the principal porosity appears at a distance of the order of $10^{-2}$ cm in cases in which diffusion has taken place for sufficiently long. It seems more likely that the pores formed initially redissolve and that the $\sqrt{t}$ law is the result of a combination of several effects.

In this connection, Barnes has found that the swelling in the direction of the diffusion gradient is between a third and a half of the Kirkendall shift in a typical specimen. A similar conclusion can be drawn for the couples of copper and alpha brass from the measurements of Bückle and Blin [5]. It would follow that between a third and a half of the vacancy current in the diffusion zone is transferred to the pores if a direct diversion of a vacancy current varying as $1/\sqrt{t}$ actually occurred.

Cyril S. Smith has pointed out to the writer that when brass is dezincified by evaporation, the channels through which the zinc emerges, and which presumably have their origin in pores, are sufficiently small that they can act selectively as semi-permeable barriers for gases, permitting small molecules to pass and holding back large ones. This observation supports the view that the pores can be very small at one stage in the diffusion process.

3. Although the preceding analysis of the Kirkendall effect indicates that in the Cu-Ni system studied by Barnes the quantity $\rho/N_t\sigma_t$ may have a value of the order of $2.5 \times 10^3$ cm, the individual estimates of $\rho$, $N_t$ and $\sigma_t$ obtained by resolving this are highly conjectural even if the important uncertainty in $R_c$ is disregarded. It would be good to have a better understanding of the individual parameters and the way in which they vary with temperature. If we assume that a value of $\rho$ of the order of 1 is not radically in error in cases in which the voids are observed, we may conclude with modest assurance that the quantity $\omega = 1/N_t\sigma_t\lambda$ is approximately $10^{11}$ provided $R_c$ is near 1. This composite quantity represents the number of jumps a free vacancy makes before becoming trapped. If the assumptions that $R_c \backsim 1$ is correct, $\omega$ apparently is not always less than $10^9$ as Bardeen and Herring hoped might generally be the case.

The evidence concerning the width of the porous zone in brass, Cu-CuAl, and Ag-Au indicates that $\rho/N_i\sigma_i$ may be larger in these cases than in CuNi. However, it does not seem safe to conclude that the values of $\omega$ are larger since the relative values of $\rho$ are not known and it is not certain that $R_c$ is the same in all materials.

Herring [private communication] has called the writer's attention to the possibilities inherent in the experiments of Kuczynski and Alexander [3]. These investigators have studied diffusion in the vicinity of the junction between a metal wire of small diameter (5 to 10 mils) and essentially flat metallic surfaces. The results are somewhat complicated since they are probably accompanied by the Kirkendall shift, at least when the two metals are different, by redeposition through vaporization and condensation and through surface migration, and possibly by plastic flow under surface tensional forces. In all cases the two sharp, cusped voids formed by tangency of circular cylinder and plane are transformed relatively rapidly to two grooves with continuous curvature, forming thereby a bonded neck between the plane and cylinder. These grooves are usually displaced in the course of diffusion in the direction that might be expected from the Kirkendall shift, although it is not evident that the Kirkendall effect is the only factor operating. In any event, the radius of curvature at the base of the grooves is of the order of $10\mu$ in many of the photographs shown in the paper. The width of the necks and of the diffusion zone is of the order of $100\mu$ in typical cases. If $\omega$ is as large as $10^{11}$, $\delta\Delta$ should be of the order of $100\mu$, whereas it is only of the order of $10\mu$ if $\omega$ is as small as $10^9$.

If $\omega$ is as large as $10^{11}$, we should expect the surface of the specimens to play an important role in determining the flow of vacancies. In particular, if $R \backsim 1$ inside the specimen we might expect the shape of the groove to show asymmetrical form since it would receive vacancies preferentially from one side, the radius of curvature not being great enough for the base of the groove to act as a source rather than a sink for values of $R \backsim 1$. On the other hand, if $\omega$ is nearer $10^9$ and if $R$ is much smaller than unity, in the stages of diffusion shown in the pictures, the base of the groove might be expected to be more symmetrical, as is observed.

Unfortunately a study of the work of Kuczynski and Alexander seems to raise at least as many problems as it solves. On the whole the grooves remain deep throughout the course of the experiment (see Fig. 3 for the case of a copper wire on nickel, for example), indicating that the grooves actually receive vacancies from the interior. Thus it is possible that vacancies are flowing to the surface in considerable number and that factors other than vacancy flow determine the shape of the groove. Moreover it is not known whether or not internal porosity exists and is the same in these specimens as in the case of planar specimens. It would be exceedingly interesting to have information on this point.

4. It is quite possible that $\sigma_i$ varies substantially with the temperature. For example it is possible that at relatively low temperatures a vacancy is trapped whenever it finds itself near a dislocation line. Thereafter it may only move along the dislocation until it finds a jog where it can disappear. On the other hand, at high temperatures, such as those used by Barnes, it is possible that the vacancy will re-evaporate from an average position on a dislocation line and is truly trapped only if captured directly at a jog. Thus it is conceivable that $\sigma_i$ could vary by a factor of the order of 1,000 from low temperatures to high. Any variations of this type in $\sigma_i$ would presumably be reflected in variation of $\rho/N_i\sigma_i$ or $\omega$.

5. At the time this is written, essentially all the couples on which extensive measurements have been reported are composed of face-centered cubic metals. It is conceivable that an exceedingly low density of sources and sinks of vacancies is one of the characteristics of well-annealed face-centered cubic metals. The density of sources and sinks for vacancies in well-annealed specimens of single crystals may vary substantially from one crystal type to another so that the ease with which pores are formed is different for different types.

Balluffi has called the writer's attention to as yet unpublished observations on specimens of beta brass containing 52 atomic per cent of zinc which have been dezincified by evaporation at 835°C in an evacuated capsule containing chips of 40 atomic per cent beta brass. Appreciable porosity was observed. Other measurements show that $D_{Zn}/D_{Cu} = 3.4$ in this case, so the Kirkendall effect is strong. Since beta brass is body-centered cubic, these results indicate that the body-centered cubic lattices probably do not behave radically differently from face-centered cubic ones.

It would be exceedingly interesting to have comparable observations on the alkali halides or on silicon-germanium specimens since these materials probably do not form partial dislocations, at least of the kind normally responsible for slip.

Evidence presented in paragraph (9) below,

dealing with observations very different from those on porosity, indicates that the density of sinks for vacancies is low in alpha iron.

6. If the preceding analysis is essentially right, one might expect to observe the Kirkendall effect without observing porosity. To speak in terms of the approximate parameters employed, the Kirkendall effect will be observed whenever $\rho$ is greater than zero, whereas a value near to, or larger than, unity is presumably needed for voids if the condition that $R_T \backsim 1$ is correct. Correa da Silva and Mehl [2] did not find voids in all specimens they studied; however, their excellent observations probably are not adequate in this respect since they did not carry out an exhaustive search for pores. It would be interesting to know if voids can be found in specimens having a relatively small Kirkendall effect. Balluffi and Alexander have found porosity in the silver-gold system which shows one of the relatively small, although by no means negligible, displacement effects.

7. Greenough [16] has recently demonstrated that diffusional viscous flow in solids, of the type postulated by Nabarro [17] for low stresses, is essentially negligible in single crystals of silver, although it is observed in polycrystals. This flow is presumed to arise from vacancy currents between grain boundaries and the surface of the specimen under the action of the applied stress. Herring [18] first predicted that the diffusional viscous flow would be negligible in single crystals on the basis of the argument that dislocations would not act indefinitely as regions where the vacancy current has non-vanishing divergence because the forces between dislocation lines would bring them to equilibrium after a relatively small amount of displacement, insufficient to produce as much plastic flow as is observed in polycrystals for similar stresses. The preceding analysis suggests an alterative or concurrent explanation: The number of independent atomic sources or sinks within the grains may be very small compared with the number at crystal boundaries, so that the sustained vacancy currents from and to the former are negligible compared with those from and to the latter, as long as the vacancy density departs only slightly from the equilibrium values, which is presumed to be the case during diffusional viscous flow.

8. Ellwood and Bagley [19] have observed changes in the density of certain binary alloy systems for appropriate compositions and have interpreted this effect as the result of the incorporation of vacant lattice sites in such a way as to fill out Brillouin zones. For example a specimen of 80Cu20Ni decreased in density by about 4.5 per cent after being annealed at 900°C for 4,175 hours. Similar effects have been observed in aluminum-zinc and gold-nickel alloys. One cannot help but wonder if this effect is attributable to porosity, similar to that accompanying the Kirkendall effect, developed as a result of diffusion which occurs during the annealing procedure and which is a consequence of gradients in composition inherent in preparation of the alloy. In fact the investigators have observed "considerable micro-porosity" near some of the grain boundaries during the heat treatment. The diffusion distance $d$ employed in the present paper would be of the order of 0.1 cm for times of the order of magnitude of those employed for heat treatment of the copper-nickel system at 900°C. It is possible that only a small fraction of the nuclei for pores, which may operate at relatively small excess concentrations of vacancies, are effective in these experiments. It is also possible that $R_e$ is generally much less than unity and that the typical nuclei responsible for the pores in the Kirkendall effect are active in Ellwood's specimens.

9. Buffington and Cohen [20] have observed that self-diffusion in $\alpha$-iron may be accelerated, at a given temperature, by applying stresses which induce creep during diffusion. The enhancement in the diffusion rate appears to be related primarily to the rate of plastic flow, the ratio $D_s/D_u$ of the diffusion coefficient $D_s$, when stresses are applied, to the coefficient $D_u$ in the unstressed specimen being $1 + c\dot{\epsilon}$ at 890°C. Here $\dot{\epsilon}$ is the strain rate and $c$ is a constant which has the value 50 when $\epsilon$ is expressed in units of hours$^{-1}$. A total strain of 0.27 was induced by creep in the typical specimen. The shortest period for attainment of this strain was approximately one hour. The diffusion coefficient in the absence of strain is approximately $4 \times 10^{-11}$ cm$^2$/sec at 890°C, the activation energy being approximately 59,800 cal per mol.

The most straightforward interpretation to give to these measurements is to assume that the lattice defects produced [15] as a result of plastic flow, at a rate proportional to the strain rate, enhance the diffusional effects caused by the thermally induced lattice defects. If we assume that the latter are predominantly vacancies, this assumption leads to most nearly consistent results if we also assume the lattice defects induced by plastic flow are predominantly vacancies, since we might expect the diffusion rate to be suppressed for small rates of strain if the thermal diffusion were the result of vacancies

whereas plastic flow induced primarily interstitial atoms.

With this assumption, we may proceed to estimate the lifetime of vacancies. If $\eta$ is the number of vacancies produced per unit strain, $\epsilon$ is the strain, $t$ is the time over which the strain is produced, $\pi$ is the jump frequency for vacancies, $N_{vt}$ is the density of thermally induced vacancies, and $\omega$ is the number of jumps a vacancy makes on the average in the course of finding a sink, we may obtain the following expression for the ratio of the equilibrium density of vacancies produced by plastic flow to the density produced thermally

$$\epsilon\eta\omega/\pi t N_{vt}.$$

We shall set this equal to the measured quantity $c\dot{\epsilon}$ giving the enhanced component of diffusivity. We may also make use of the relation $D_u \cong N_{vt}\pi\lambda^2/N$, where $N$ is the density of atoms and $\lambda$ is the atomic spacing, and give this combination of parameters its experimental value for 890°C, cited above. Since $\epsilon/t$ is the average strain rate, we readily find

$$\omega = cND_u/\eta\lambda^2.$$

Taking $\lambda^2 = 10^{15}$ cm$^2$, $N = 9 \times 10^{22}$, and $\eta = 2 \times 10^{19}$ per cc, the latter being a conservatively small value, we find

$$\omega \backsim 10^{13}.$$

This value of $\omega$ is large compared with values of the order of $10^{11}$ and $10^{12}$ obtained for other materials by the means described in preceding paragraphs. There is, however, enough uncertainty both in the arguments employed and in the values of the parameters used in deriving $\omega$ that the value cannot be accepted as reliable or final, but merely as suggestive.

If we assume that the activation energy of approximately 60,000 cal/mol found for $\alpha$-iron may be divided into a value of 40,000 cal/mol for the generation of vacancies and a value of 20,000 cal/mol for the migration of vacancies, the equilibrium density of vacancies at 890°C is found to be about $10^{17}$ per cc, whereas the jump frequency is about $10^{10}$/sec. If the second of these quantities is approximately correct, the value $\omega \backsim 10^{13}$ implies that the lifetime of vacancies is of the same order as the time of creep in the more rapid experiments.

The maximum relative increase in diffusion rate observed by the investigators is about 15. One must conclude that the density of vacancies achieves values of the order of 15 above the thermal equilibrium density during the most rapid deformations, if the interpretation of this enhancement in terms of the production of vacancies by plastic flow is correct. Presumably an appreciable fraction of these vacancies should precipitate in such a way as to form voids, if the principles used in the explanation of the voids observed in connection with the Kirkendall effect are also applicable in the present case. Since the total strain was 27 per cent, of the order of $5 \times 10^{18}$ vacancies per cc should be produced, provided the conclusions drawn [15] for the case of copper are valid for iron. It would be interesting to know if porosity is observable.

We would face difficulty in understanding a value of $\omega$ as large as that calculated above in the deformed diffusion specimens if interstitial atoms are produced by plastic flow in numbers comparable to vacancies, for one might expect $\omega$ to drop to values near $10^6$ if $10^{17}$ interstitial atoms are present. On the whole, a consistent interpretation of the Buffington-Cohen experiment along the lines discussed here appears to require that creep produce predominantly the defect responsible for normal thermal diffusion. This conclusion is very remarkable in itself, if further research sustains it, for it suggests that the vacancies which enhance the diffusion coefficient in the Buffington-Cohen experiment may be generated thermally rather than geometrically, that is, under circumstances which markedly favor the imperfection which has the lowest energy of formation. This, in turn, suggests that the mechanism by which vacancies are produced during plastic flow at elevated temperatures may not be the same as that which operates at lower temperatures.

The writer is indebted to several friends and colleagues for critical comments concerning this work. Particular mention should be given to Drs. Conyers Herring, R. S. Barnes, R. Balluffi, and L. Slifkin.

## Appendix

We shall consider, in a somewhat idealized manner, the equations governing the accumulation of vacancies at the edge of the diffusion zone and their solutions.

The rate at which vacancies accumulate in a unit volume of the crystal may be expressed in the form

$$\frac{\partial N_v}{\partial t} = -\operatorname{div} I_v + \frac{1}{T}(N_{vo} - N_v) \tag{24}$$

in which $-\operatorname{div} I_v$ is the increase in density as a result of flow of vacancies, $N_{vo}/T$ is the rate of spontaneous generation of vacancies, with $N_{vo}$ the equilibrium density of vacancies and $T$ the lifetime, and $N_v/T$ is the rate of decay of vacancies at traps.

For simplification, we shall assume that $T$ and $N_{vo}$ are constant throughout the specimen. Actually $T$ may be dependent upon the history of the material and may vary both from position to position, and as a function of $N_v$, increasing with increasing values of the latter. Moreover, $N_{vo}$ will usually be a function of chemical composition.

$I_v$ may be taken in the form

$$(25)\quad I_v = -D_v \operatorname{grad} N_v + N_v\left(\frac{\partial \pi}{\partial N}\right)\lambda^2 \operatorname{grad} N_a$$

(see Equation (5)) in which $D_v$ is the diffusion coefficient for vacancies. We shall simplify the problem further by the following assumptions: (1) the diffusion gradient is in the $x$ direction; (2) the system is in a steady state so that $\partial N_v/\partial t = 0$; $(\partial\pi/\partial N)$ may be replaced by the approximate form $\rho\pi/N_a$ (see Equation (9)). The equation for $N_v$ then becomes

$$(26)\quad D_v\frac{d}{dx}\left(\frac{dN_v}{dx} - \frac{\rho}{Ndx}\frac{dN_a}{dx}N_v\right) + \frac{1}{T}(N_{vo} - N_v) = 0.$$

The procedure of treating the chemical gradient as if it were instantaneously fixed and seeking a stationary-state solution for the vacancy density is justifiable as long as $D_v$ is far larger than the chemical diffusion coefficient $D_c$, which is normally the case. Under these circumstances, the chemical gradient will not change appreciably during the time $T$ in which the vacancies come to equilibrium.

The quantity $dN_a/dx$ is normally a continuous function of $x$. For example, if the chemical diffusion coefficient is a constant, $D_c$, and if diffusion is not appreciably affected by the presence of voids, $dN_a/dx$ is

$$(27)\quad \frac{dN_a}{dx} = \frac{\Delta N_a}{\sqrt{(\pi d)}}\exp\left(-x^2/4D_c t\right)$$

in which $\Delta N_a$ is the total difference in composition on both sides of the couple and $d = 2\sqrt{(D_c t)}$.

Whenever $dN_a/dx$ is a function of $x/d$, (26) may be expressed in the form

$$(28)\quad \frac{d}{dy}\left(\frac{d\phi}{dy} - f(y)\phi\right) + \frac{d^2}{D_v T}(1-\phi) = 0$$

where $y = x/d$, $\phi(y) = N_v(x)/N_{vo}$ and $f(y) = (\rho/N_a)(\partial N_a/\partial y)$. The coefficient of $(1-\phi)$ in the last term evidently is $(2d/\delta\Delta)^2$, where $\delta\Delta$ (Equation (18)) measures the dispersion of the vacancies as a result of Brownian motion after time $T$.

The boundary conditions to be placed upon $\phi$ are continuity of this function and its first derivative if the function $f(y)$ is continuous. Othedrwise $\phi$ an the vacancy current (25) should be continuous at points of discontinuity in $f(y)$.

It is possible to obtain a simple analytical solution of Equation (28) in the case in which the gradient of $N_a$ is assumed to be constant in a region of width $d$ and is taken to be zero everywhere else. In the regions where $f(y)$ is zero, (28) takes the form

$$(29)\quad \frac{d^2\phi}{dy^2} + \gamma^2(1-\phi) = 0$$

whereas in the region where $f(y)$ is constant

$$(30)\quad \frac{d}{dy}\left(\frac{d\phi}{dy} - 2a\phi\right) + \gamma^2(1-\phi) = 0$$

where $\gamma^2 = d^2/D_v T$ and $2a = \rho\Delta N_a/N_a$.

If we assume that the discontinuities occur at $y = \pm\frac{1}{2}$, the form of $\phi$ in the various ranges is as follows

(a) $y < -\frac{1}{2}$

$$(31)\quad \phi = 1 + A\exp(\gamma y)$$

(b) $-\frac{1}{2} < y < \frac{1}{2}$

$$(32)\quad \phi = 1 + C\exp(\omega_1 y) + D\exp(\omega_2 y)$$

(c) $y > \frac{1}{2}$

$$(33)\quad \phi = 1 + B\exp(-\gamma y)$$

where $\gamma$ is the positive root of $\gamma^2$ and

$$(34)\quad \omega_1 = a + \sqrt{(a^2+\gamma^2)},\qquad \omega_2 = a - \sqrt{(a^2+\gamma^2)}.$$

It may be noted that $\gamma$ measures the relaxation distance outside the diffusion zone, whereas $2a/\gamma^2$ is the distance, in units of $d$, which a vacancy migrates in the diffusion zone before being captured. When $2a/\gamma^2$ is one or greater, the vacancies go the entire distance.

Applications of the appropriate boundary conditions lead to the relations

$$(35)\quad C = 2a\times\frac{\gamma\cosh(\omega_2/2) - \omega_1\sinh(\omega_2/2)}{2\gamma^2\sinh[(\omega_1-\omega_2)/2] + \gamma(\omega_1-\omega_2)\cosh[(\omega_1-\omega_2)/2]},$$

$$D = -2a\times\frac{\gamma\cosh(\omega_1/2) - \omega_2\sinh(\omega_1/2)}{2\gamma^2\sinh[(\omega_1-\omega_2)/2] + \gamma(\omega_1-\omega_2)\cosh[(\omega_1-\omega_2)/2]}.$$

$A$ and $B$ may be evaluated from the relations

$$(36)\quad A = C\exp((\gamma+\omega_1)/2) + D\exp((\gamma+\omega_2)/2),$$
$$B = C\exp((\gamma-\omega_1/2) + D\exp((\gamma-\omega_2)/2).$$

A number of interesting cases may be considered:

(a) $a = 1$, $\gamma = 1$.

Since the ratio $2a/\gamma^2$ measures the distance the vacancies migrate in the diffusion zone, this case

represents an example in which the vacancies drift through the zone on the average and in which $a$ and $\gamma$ have what might be termed intermediate values.

We readily find $\omega_1 = 2.41$, $\omega_2 = -0.41$, $C = 0.304$, $D = -0.487$. The values of $\phi$ at the boundary points are

$$\begin{aligned} &\phi = 1.62 \text{ at } y = \tfrac{1}{2}, \\ &\phi = 0.49 \text{ at } y = -\tfrac{1}{2}. \end{aligned} \tag{37}$$

Thus there is a 62 per cent excess of vacancies at the positive boundary point, to which vacancies are pumped, and a 51 per cent deficit at the negative boundary point. It is evident that the maxima and minima of $\phi$ occur at these points.

(b) $\gamma$ very large compared with unity and with $a$.

This corresponds to a case in which $d/\delta\Delta$ is large and in which the vacancies do not migrate throughout the diffusion zone in one lifetime so that we might expect the Darken-Bardeen situation to be most nearly realized. We find

$$\begin{aligned} &\omega_1 \to \gamma + a \to \gamma, \quad \omega_2 \to -\gamma + a \to -\gamma, \\ &C \to \frac{a}{\gamma}\exp(-\gamma/2), \quad D \to -C. \end{aligned} \tag{38}$$

Thus $\phi \to 1 \pm a/\gamma$ at $y = \pm \frac{1}{2}$, respectively, and the deviations from unity are small.

(c) $a$ large compared with unity and $\gamma$.

$$\omega_1 \to 2a, \quad \omega_2 \to -\gamma^2/2a,$$

$$C \to a\frac{1 + \gamma/2}{\gamma \sinh a + a \cosh a} \to \frac{1 + \gamma/2}{\cosh a},$$

$$D \to -a\frac{\cosh a + (\gamma/2a)\sinh a}{\gamma \sinh a + a \cosh a} \to -1.$$

The values of $\phi$ at the two boundaries are

$$\begin{aligned} &\phi \to 2 + \gamma \text{ at } y = \tfrac{1}{2}, \\ &\phi \to 2\exp(-2a) \text{ at } y = -\tfrac{1}{2}. \end{aligned} \tag{39}$$

Thus the specimen is essentially depleted of vacancies at the negative boundary, whereas the excess concentration is $1 + \gamma$ at the positive junction. This evidently corresponds to a case in which the Kirkendall effect is very strong and in which a relatively large excess of vacancies accumulates at the positive boundary.

It is interesting to note that in case (c) the value of $\phi$ at $y = \frac{1}{2}$ increases linearly with $\gamma$, which is proportional to $d$. Thus when $a$ is large, the concentration of vacancies increases during the diffusion process until $\gamma^2$ becomes comparable to $a$, or until $2a/\gamma^2$ becomes comparable to unity. Thereafter, we may expect the maximum of $\phi$ to decrease with increasing $d$, in accordance with case (b). Thus, in this repect, the foregoing solution bears out the conclusions drawn on more qualitative grounds in the text. We may note, however, that for small values of $\gamma$, $\phi \to 2$ at $y = \frac{1}{2}$ according to (39). Thus the density of vacancies at this point is twice the equilibrium value even when $d$ is small, in contrast with the value $\phi = 1 + R_t \to 1$ for small $d$ anticipated in Section III. The difference evidently arises from the assumption, contained in Equation (28), that the equilibrium density of vacancies is the same on both sides of the couple. As a result, an appreciable numper of vacancies found at $y = \frac{1}{2}$ originate at regions where $y < -\frac{1}{2}$ when $a$ is large. In computing $R_t$ in Section III, in contrast, it was assumed that the extra vacancies found at $y = \frac{1}{2}$ originate entirely in the diffusion zone. The latter assumption is probably much more realistic for the couples studied experimentally thus far.

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