"DIFFUSION RATE ALONG TWO PHASE, INTERPHASES AND THE INFLUENCE OF THEIR RATE OF DIFFUSION ON TRANSFORMATION RATE."

相與相間擴散速率及其影響因子之研究

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I. Introduction

The phenomenon of diffusion is of great importance in metallurgy from both the theoretical and practical points of view. Apart from its own intrinsic interest, it demands attention because of the fact that many phase changes in alloys involve a redistribution of the various kinds of atoms present, and the rates of such changes are controlled by the speeds of migration of the participating atoms.
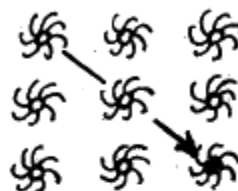
II. Basic ideas and theories

As the temperature of an alloy lattice is raised above the absolute zero of temperature, atomic motion of two kinds can be observed. The first of these is vibration of the atoms about their equilibrium positions in the crystal lattice. In Fig. (a) the relative slightly vibration that occurs at moderate temperatures is indicated by short lines extending from the equilibrium position of each atom. Vibration can take place without appreciable diffusion or gross movement of atoms. Diffusion, the second type of atomic motion that can occur, is shown schematically in Fig. (b) During diffusion certain atoms change their positions in the crystal lattice with respect to neighboring atoms. It seems evident that atomic vibration is necessary in order that diffusion take place, and as the amplitude of atomic vibration increases with increasing temperature, the rate of diffusion also increases.
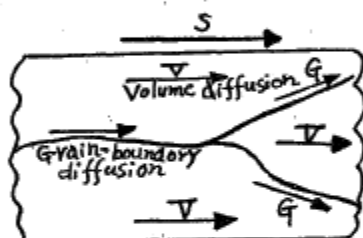
● 　Solute atom

○ 　Solvent atom

(a) Atomic vibration at moderate temperatures.

(b) Rapid diffusion associated with atomic vibration at higher temperatures.

Surface diffusion

(c) Illustration of surface, grain-boundary, and volume diffusion.

In Fig. (c) three different types of diffusion are indicated. Although the specific rates of surface and grain boundary diffusion are much higher than the rate of volume diffusion, their actual contribution to the total diffusion process is usually small because of the small numbers of atoms in the surface and grain boundary regions.

The first Fick's law:

The basic equation for all diffusion phenomena in metals is the first Fick's law.

$$dm = D\frac{\partial c}{\partial x} \; Adt\cdots\cdots(1).$$

Where dm = the number of grams of metal that cross a plane perpendicular to the direction of diffusion; D = a diffusion coefficient whose value depends on the metallic system being considered (its units are cm^2/sec); A = the area (in cm^2) of the plane across which diffusion is occurring; dt = the time in seconds during

which diffusion occurs; $\frac{\partial c}{\partial x}$ = the concentration gradient that exists at the plane in question (the concentration, c, is expressed in grams per cubic centrimeter). The minus sign appears in equation (1) in accordance with the fact that a negative concentration gradient causes diffusion to occur in the positive direction. In the absence of a concentration gradient no net transfer of metal across the plane can occur.

The second Fick's law:

The first Fick's law is not in a convenient form for the treatment of many diffusion problems. By means of a derivation that takes into account the net gain of atoms in a vanishingly small volume, it is possible to obtain the second Fick's law. Although the most general form of this law is complex, a simpler version is often adequate. For example, the equation $\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial X^2}$ ....(2) in which D is assumed to be constant, satisfactorily describes diffusion of small concentrations of an interstitial or substitutional solute in a solid solution. This form of the second Fick's law will be used in the remaining considerations of diffusion phanomena.

III. The mechanism of diffusion in metals

There are three reasonable mechanisms by which a given atom of type B may diffuse relative to atoms of type A in a given lattice, namely: (1) The atoms A and B may interchange places. (2) B atoms may diffuse through the interstices of the lattice, (3) B atoms may diffuse as the secondary result of the diffusion of vacancies through the lattice.

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A A B A A        A A B A A        A A B A A

B A A B A        B A A B A        B A A B A

A B A B A        A   A B A        A B → B A

A A B A A        A A B A A        A A B A A

B A A B A        B A A B A        B A A B A
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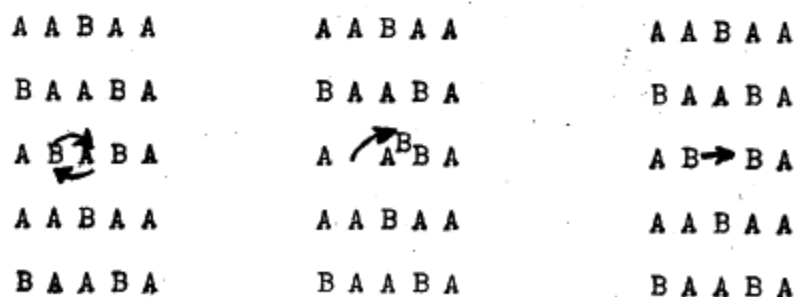
Fig. (d) The three mechanisms of diffusion. There has been considerable speculation concerning the actual mechanism of diffusion in particular cases. It

seems almost beyond doubt that the first machanism does not occur because the force required to squeeze two atoms by one another in a closely packed lattice is too large. It also seems beyond question that the diffusion of the ineterstitial component in interstitial alloys, such as carbon in steel, takes place by means of the interstitial diffusion mechanism. The mechanism by which diffusion occurs in substitutional alloys is still open to question. Estimates of the relative magnitudes of the forces incurred in the interstitial and vacancy diffusion processes, however, indicate that the vacancy mechanism is definitely more likely.

IV. Phenomena of diffusion rate along two phase, interphase boundaries.

We have seen the basic ideas, theories and mechanisms of diffusion in the above section.

This raises two questions:

(1) How the diffusion phenomenon occurs along two phase, interphase boundaries of both in the same chemical composition and different chemical composition structures?

(2) Upon what reasons this phenomenon would be explained? In order to understand and offer satisfactory answer about this two questions, first study will be made about the effect of orientation of the grains in the microstructure of the same chemical composition. The relative orientation of the grains on either side of a grain boundary can control the surface energy of the boundary. Where this is the driving force for grain-boundary migration, the rate of growth may be controlled by the relative orientation. The orientation of the grains forming the boundary also controls the structure of the boundary, and the rate of growth may be influenced for this cause. When boundaries migrate, atoms at the boundary must move to new positions, and in doing so must occasionally move past other atoms much as in diffusion. Qualitatively one would expect the energy barrier for movement to be high if the disregistry between the grams 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, and thus the activation energy for atom movement should be lower and the rate of boundary

migration higher.

There is a considerable body of evidence that this is true, and 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. Many kinds of boundaries are found in metals. They may separate domains which differ in crystal structure and chemical composition (phase boundaries), or they may separate domains which differ only in crystallographic orientation (grain boundaries). The migration of boundaries between domains which differ in chemical composition requires that at least some of the atoms move many interatomic distances by diffusion. This slow process will frequently be rate controlling. On the other hand. The migration of grain boundaries requires that most of the atoms move only small distances to extend one of the orientation domains. Most of the atoms need not even change their neighbors. Diffusion in the ordinary sense does not control the rate of the process. At the present time we shall consider exclusively the diffusion phenomenon of very sharp boundaries between domains which differ primarily in chemical composition and crystallographic orientation. If the same composition microstructure will be taken, boundaries between grains which are of quite different orientation (some certain plane), migrate very much more rapid than that of small disregistry. The diffusion rate along interphase (grain boundary) is very much more rapid than those within the individual grain. The grain boundary diffusion overtakes the volume diffusion and reaches a max. at 45 degrees. It was concluded that rapid grain boundary diffusion occurs only in areas of highly distorted lattice. This could be explained in such a way that the vacancies are more available along interface than those within the individual grains. In other words, the dislocation is much more easier to establish along grain boundary than that within the individual grains. If evidence will be taken about the diffusion in the different composition grain and grain boundary, the following concepts have to be studied.

In view of the principle and the fact that the body-centered cubic lattice is a less closely packed arrangement of atoms than the face-centered cubic lattice, one could expect that there would be much more difference between the mobility of atoms in the grain and in the grain boundary of a body-centered cubic lattice than in a faced-centered lattice. If such is the case, one might also believe that preferential grain-boundary diffusion would occur to a higher degree, if at all, in the body-centered cubic material than in the face-centered cubic material. One

sees, then, that the determining factor in equilibrium microstructures is the relation between the energy of the interface and crystal grains of one and the same composition and structure.

In the two-phase nature system, different in chemical composition and. microstructure, a study will be taken about the diffusion rate along two phases and phase boundary (very sharp). According to the above principle, the relative orientation of the grains on either side of a phase boundary is quite much more different than that of the same composition structure. In other words, the diffusion rate along individual grain and phase boundary is quite much more different than that in the same composition structure. I would see that the diffusion rate along sharp phase boundary is more rapid than that in the same chemical composition. Because of the importance of the allotropic transformation of iron for body-centered cubic to face-centered cubic at high temperatures, the effect of this change in crystal structure on the rate at which solute atoms diffuse in iron has been studied. At a given temperature these diffusion processes and self-diffusion of the iron occur about one hundred times more rapidly in ferrite (body-centered cubic) than in austenite (face-centered cubic). The diffusion of carbon in alpha iron, however, is much more rapid than in gamma iron. Wells and Mehls report the diffusion of carbon (in the range of 0.01%) in gamma iron as $D = 0.07e^{\frac{32,000}{RT}}$. The diffusion of carbon in alpha iron can be represented by the equation: $D = 7.9 \times 10^{-3}e^{\frac{18,100}{RT}}$. The diffusion of carbon does not appear to be affected by grain size, deoxidation or small additions of silicon and cobalt.

V.　Factors influencing the diffusion rate

The diffusion coefficient, D, is generally not a constant. Ordinarily D is a function of many variables such as temperature, concentration, and crystal structure. In a given instance all of these variables are assumed to have specified values, and the diffusion coefficient then is a definite number. However, in arriving at this number it is frequently necessary to consider the individual effects of one or more of these variables.

(a) *Temperature:* An idea of the tremendous influence of temperature on diffusion is given by the rule of thumb that the diffusion constant doubles for every twenty-degree centigrade increase in temperature. More exactly the diffusion constant is related to the absolute temperature (°C+273) by the equation, $D =$

$Ae^{-\frac{Q}{RT}}$ where A, Q, and R are independent of temperature. When the "activation energy," Q, is given in calories per gram mol, then the gas constant, R, has the value 1.987 calories per gram mole per degree kelvin. The "frequency factor." A, is related to the frequency of vibration of the diffusing atoms, while Q is a measure of the energy barrier that tends to prevent diffusion from occurring. Values of A and Q for the determination of an approximate diffusion coefficient in several binary systems are given in the following table:

Approximate values of A & Q for several diffusion systems

Diffusing metal	Matrix metal	A cm²/sec	Q Calories per gram mole
Carbon	γ-iron	0.21	33,800
Carbon	α-iron	0.0079	18,100
Iron	α-iron	5.8	59,700
Iron	γ-iron	0.58	67,900
Nickel	γ-iron	0.5	66,000
Manganese	γ-iron	0.35	67,500
Copper	Aluminum	2.0	33,900
Zinc	copper	0.033	38,000

(b) **Concentrotion:** Few data are available on the variation of diffusion coefficient with concentration. However, in general, a marked change in the value of the coefficient occurs with change in concentration. The effect of concentration is more easily studied in interstitial solid solutions, since the effect of the diffusion of the solvent atom can be neglected.

(c) **Crystal structure:** Effect of crystal structure is the variation of the diffusion coefficient with crystal direction in a single crystal of the solvent metal. Such anisotropy is nearly or completely absent in cubic metals, but bismuth (rhombohedral space lattice) shows a ratio of about one thousand in its self-diffusion constants measured parallel and perpendicular to the c-axis. Moreover, if a crystal structure is distorted either by elastic strains or by extensive plastic deformation, the rate of diffusion is generally increased.

(d) **Impurities:** The presence of small amounts of additional metals ususally has a relatively small effect on the diffusion of solute atoms in a solvent metal.

This fact is often useful in treating problems in which diffusion is only one of several possible variables. For example, it can be concluded that the strong influences of alloying elements on the hardenability of steel must be the result of factors other than large changes in the rate of carbon diffusion.

(e) **Grain size:** Since grain boundary diffusion is faster than that within the grains, it is to be expected that the over-all diffusion rate would be higher in a fine-grained metal. However, in the usual range of grain sizes it is generally not necessary to take grain size into account in making diffusion calculations.

VI. Influence of diffusion rate on transformation rate

It is generally agreed that the rate of growth is controlled by the rate of diffusion of solute in the vicinity of the interface, and that the accompanying crystallographic changes occur as fast as the necessary redistribution of solute will allow. It is to be remarked, however, that since diffusion takes place only be virtue of a composition or more precisely, an activity gradient, any system in which diffusion occurs is not at equilibrium; consequently, reasoning based on an equilibrium diagram alone cannot be strictly valid. It is here, assumed, that equilibrium prevails locally even though the system as a whole is far from equilibrium-in other words, that diffusion is slow compared with the rate of reaction to form a new phase. This assumption is reasonable in many cases, though not in all-for instance, the austenite-pearlite transformation under many conditions.

Mehl and Rhines have measured the rates of the simultaneous diffusion of Ni and silicon into copper and compare these rates with those of each of these elements diffusing individually into copper. At a concentration less than 1%, the diffusivity is not greatly affected by the simultaneous diffusion of the other element. At higher concentrations the rate of diffusion of the more repidly diffusing silicon is markedly decreased by the presence of nickel, where as that of the more slowly diffusing nickel is influenced but little, if at all, by the presence of silicon. Although this is not the place for an extended discussion of this complex phenomenon, it is perhaps worthwhile to point out the bearing of equilibrium considerations on diffusion.

It is commonly stated that diffusion of an element occurs by virtue of its concentration gradient. Clearly, this is not strictly so, for two phases in equilibrium may be placed adjacent to each other without the occurrence of diffusion,

although there may be an infinitely great gradient (discontinuity) of concentration at the interface. From the view-point of phase equilibrium this is obvious that it need hardly be mentioned, for the definition of equilibrium precludes the possibility of interdiffusion between phases that already are in equilibrium. Thus, cementite (Fe_3c) in intimate contact with austenite saturated therewith exhibits no tendency to lose carbon to the austenite; in fact, austenite supersaturated with respect to cementite tends to lose carbon to produce this higher-carbon phase -- that is, carbon diffuses from a region (cementite) where it is present at a lower concentration to a region (cementite) where it is present at a higher concentration. The rule that diffusion takes place in the direction of lower concentration applies at best only to a single-phase region; thus, it is true that carbon diffuses in the austenite in the direction of lower carbon concentration, which is toward the austenite-cementite interface. For any one phase of a binary system this rule is valid and is expressed quantitatively by Fick's law, modified if necessary to allow for variation of the diffusion coefficient with concentration.

VII. Industrial applications of diffusion principles

(a) **Metal bonding:** A good example of an industrial application of diffusion principles is the bonding of metals, which includes such processes an galvanizing, soldering, and metal-cladding. Although a continuous metallic bond may be formed under many different conditions between two different metals, in every instance it is necessary that some diffusion occur. Since diffusion can take place only in a solid solution, only two metals that have appreciable solid solubility can be bonded. Thus, because lead is practically insoluble in iron it is possible to heat steel in molten lead baths without danger of forming an adherent lead layer on its surface. The opposite problem arises when it is desirable to protect sheet iron with a thin coating of lead. In order to obtain adequate bonding it is necessary to add to the molten lead a small amount of a second metal that alloys with iron. The most popular addition is tin, and the resulting alloy is widely used in making terne plated sheet steel for roofing.

A complicating factor in some bonding processes is the presence of brittle intermetallic compounds between the two metals being joined. When diffusion occurs between two metals the primary solid solutions are formed; and in addition, those intermediate phases that exist at the diffusion temperature also form.

This behavior is illustrated for the coating of steel with zinc to produce a galvanized sheet. The galvanized coating is produced in about fifteen seconds, while the carefully prepared sheet steel is passed through a molten zinc bath at 450°C. During this time the three intermediate solid phases occur. Two-phase regions do not form in the course of the growth of diffusion bands; they merely constitute the interface between the one-phase regions. The resistance to flaking of a galvanized sheet when it is bent is improved by decreasing the amount of the brittle intermediate phases present. This can be accomplished by decreasing the total coating thickness or by adding a suitable alloying element, such as aluminum, to the molten zinc bath.

Many different methods are used to attach a layer of one metal to a different base metal. In making Alclad or Purecled sheets, a protective layer of pure aluminum is bonded to a strong aluminum alloy by hot rolling a "sandwich" made of slabs of the two materials. Care must be taken to prevent excessive diffusion in this case, since the good corrosion resistance of the pure aluminum is lost if it is contaminated by the additional elements present in the strong alloy. No problem of brittle compound formation is met in producing Alclad, but when a layer of copper is to be attached to aluminum, special precautions must be taken to insure a ductile product. One successful procedure involves hot rolling the bimetal combination to disintegrate the brittle layer as it begins to form.

(b) *Homogenization:* A Chemically inhomogeneous solid solution tends to become homogeneous through diffusion. This process has a venishingly small rate at low temperatures, however, and in practice a special heat treatment is used to produce homogenization. In many commercial alloys homogenization is achieved rather easily. In some instances the diffusion coefficient of the alloying element plays a decisive role. Thus, at a moderate temperature the rapid diffusion of zinc in copper produces effective homogenization of case brasses, while at the same temperature nickel diffuses so slowly in copper that it is difficult to eliminate segregation in cast cupronickels. Only by plastically deforming cupronickels and thereby decreasing the diffusion distance can rapid homogenization be obtained at this temperature.

As an example of the application of diffusion data to the problem of eliminating chemical inhomogeneity, the subject of bonding in steel will be considered. The use of the term "bonding" to describe chemical heterogeneity in rolled steels arises from the presence of closely spaced light and dark bonds in the

microstructure of some of these steels. These bonds represent areas of segregation of alloying elements during freezing of the ingot. During rolling the segregated and compressed into narrow bands. This segregation can be eliminated only if the alloying elements diffuse from regions in which their concentration is high to regions in which their concentration in low.

The mathematical treatment of diffusion between adjacent regions of high and low alloy content is simplified if it is assumed that the alloy concentration various sinusoidally with distance about the avarage value, so that $C=Cm \sin \frac{\pi X}{L}$ ....(3) where C=the variation from the average concentration at the point x, Cm= the initial maximum variation from the average concentration, x= the distance in centimeters, L= the distance between a region of maximum concentration and an adjacent region of minimum concentration. Using this expression for concentration, it can be shown that a solution of the second Fick law (equation 2) is $C=Cm \sin\frac{\pi X}{L} e^{\frac{\pi^2 Dt}{L2}}$ ....(4). In this equation, Cm is a constant. $\sin\frac{\pi X}{L}$ represents the sinusoidal variation of concentration that was assumed in using equation (3). For the present purpose only a maximum value of this function need be considered; that is, $\sin\frac{\pi X}{L}$ can be set equal to unity. Evidently, then, the factor that controls the decrease in degree of inhomogeneity with increasing time, t, is $e^{\frac{\pi^2 Dt}{L}}$, which decreases from unity towards zero with increasing time. Thus, the time required to produce a given degree of homogentization increases with the square of the diffusion distance, L and is inversely proportional to the diffusion constant, D, of the segregated alloying element. If bonding due to manganese segregation occurs, it is extremely difficult to produce effective homogenization in large ingots because of the large diffusion distance involved. After the ingot has been rolled, the value of L in equation (4) is reduced to about 0.003 cm, and diffusion is greatly accelerated. However, many hours of heating at an excessively high temperatur (1200°C) are required to remove bonding even in this case.

VIII. Conclusion

(a) It has been shown that the rate of growth may be predicted from the knowledge of diffusion constants, phase relations, and the interphase boundaries conditions.

(b) Large apparent deviations from Fick's law may be expected in systems of

more than two components, defined in terms of concentration. It is suggested that activity gradient rather than the concentration gradient be regarded as the "driving force" in diffusion, for since activity is successfully used instead of concentration in interpreting equilibrium, it should have like merit in interpreting the approach to equilibrium by diffusion.

BIBLIOGRAPHY

Books

1. C. Wagner: Thermodynamics of Alloys, 1952
2. Darken I. Gurry: Physical Chemistry of Metals, 1953
3. Bruce Chalmers: Progress in Metal Physics, V1, V3, V4
4. A. H. Cotrell: Theoretical Structure Metallurgy, 1955
5. F. Seitz: Physics of Metals, 1943
6. Albert G. Guy: Elements of Physical Metallurgy, 1951
7. Charles Kittel: Introduction to Solid State Physics, 1956
8. F. Seitz: Phase Transformation in Solids, 1951
9. H. B. Huntington: Atom Movements, ASM, 1951
10. C. S. Barrett: Structure of Metals, 1952
11. W. Boas: Physics of Metals and Alloys, 1947
12. R. M. Barrer: Diffusion in and through Solids, 1941

Articles

1. W. A. Johnson, Trans. TIME, 166, 114 (1946)
2. L. S. Darken, Trans. AIME, 175, 184 (1948)
3. F. N. Rhines & R. F. Mehl, Trans. AIME, 128, 185 (1938)
4. A. D. Smigolskas & F. O. Kirkendall, Trans. AIME, 171, 130, (1947)
5. R. F. Mehl & F. N. Rhines, Trans. AIME, 137, 301, (1940)
6. L. S. Darken, Vrans. AIME, 150, 157 (1942)
7. F. N. Rhines, W. A. Johnson & W. A. Anderson, Trans. AIME, 147, 205 (1942)
8. L. S. Darken, Trans. AIME, 180, 430 (1949)
9. J. Bardeen, Phys. Rev. 76, 1403 (1949)
10. Acta Metallurgica, V. 3, No. 2, P. 130-134, 170-181, March, 1955