

THE INFLUENCE OF COLD-DEFORMATION  
ON THE DIFFUSION AND SOLUBILITY OF  
INTERSTITIAL IMPURITIES (H,C) IN METALS  
( $\alpha$ -Fe,Ni) AND ALLOYS (STEELS)

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## ABSTRACT

The problem of impurity diffusion accompanied with segregation phase nucleation on dislocations has been considered using the approximation of the local equilibrium with respect to the impurity distribution between the matrix solution and the near-dislocation regions. It has been shown that the known experimental data on diffusion and solubility of interstitial impurities (C, H, ... etc.) in some metals ( $\alpha$ -Fe, Ni) and alloys (Fe-3.5% Si, Fe-0.16%C (steel)) are described in the frame work of the dislocation trap model, the only case where some segregation phases with negligible diffusion conductivity and high capture ability for impurities in the near-dislocation regions are nucleated. The characteristics of the segregation phase regions near-dislocations have been obtained from the treatment of the diffusion and solubility data. On the basis of the crystallographic and thermodynamic considerations it has been shown that the existence of such segregation phase regions along dislocation in the systems in question is possible.

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## INTRODUCTION

Diffusion is the process by which matter is transported from one part of the system to another as a result of random particle motion. It is a Kinetic process which in particular brings about the thermodynamic equilibrium of the solubility of impurities (solute) in the matrix (solvent) considered. The significance of diffusion in solids is determined, at least, by the following three aspects.

Firstly, diffusion is an elementary process which is realized at the atomic level. Therefore, the studies of diffusion in many relations is a unique way of investigating crystal structure, crystal defect--- etc. Moreover some information could particularly be obtained about the structure and properties of the near-dislocation regions from such diffusion studies. This possibility will be illustrated in this work.

Secondly, diffusion is one of the most common processes in solids. Diffusion proceeds in pure metals and metal alloys, oxides and intermetallic compounds, dielectrics and semi-conductors in a wide range of real temperatures and external conditions, such as deformation. Again the influence of such conditions will be considered in this paper.

Thirdly, diffusion plays a leading role in many processes used to determine the structure and properties of materials. Among them are some phase transformations, such as crystallization and recrystallization, processes of precipitation and coagulation, sintering of powdered materials, corrosion and oxidation processes, some mechanisms in semi-conductors (p-n junctions, etc...), and some technologically important processes of deformation and destruction of metal materials at high temperatures.

The above consideration shows in particular the great role of diffusion in the processes of the manufacturing, exploitation and destruction of materials.

Some of the most important and useful materials for the technological development achieved in this century, are steels and some alloys, based on Ni, Mo, Nb--- etc. The addition of small concentration of thermodynamically active elements (impurities) or alloying components to these alloys, have a big influence on their technological utility strength properties. In this work, more emphasis has been put on the interstitial impurities in metals such as C in Fe, C in Fe-3.5 wt% Si, H<sub>2</sub> in Fe-0.16 wt% C and D<sub>2</sub> in Ni. These impurities interact with lattice discontinuities in the matrix and change the properties of the alloys under consideration. For instance, C changes Fe to steel, which has completely different technological advantage and strength properties. Thus from these view points, it is worth to study the solubility and diffusivity of impurities

(interstitial) in metals and alloys for academic and technological purposes.

With regard to hydrogen embrittlement susceptibility, the study of the interaction between dissolved hydrogen atoms and lattice discontinuities such as vacancies, dislocations, grain boundaries, voids particle matrix interfaces or foreign interstitial and substitutional atoms in iron and other metals is of great importance from both technological and academic points of view. Thus the influence of hydrogen trapping on hydrogen diffusivity and solubility has been studied by a number of investigators [1-11], by assuming that the traps in the cold-worked metals are mainly attributed to dislocations and their stress field with an effective capture radius [13]. Because hydrogen trapping behaviors are closely related to the resistance or susceptibility to hydrogen embrittlement of steel and so much remains to be understood, there has been a continuing interest in these topics by many investigators [14].

There has been a considerable number of work devoted to interstitial hardening in body-centered cubic metals, specially iron, due to the impurity interaction with dislocations, and the interpretation in terms of the Cottrell Mechanisms is generally satisfactory. There remains, however, certain discrepancies between the predictions of the theory and experimental results. The effects at the yield point do not depend only on the simple lock-

ing of individual dislocations since crystal size and surface condition play important roles in the phenomenon [15, 16].

The corrosion process is a serious problem at present. About 25% of what is produced, is destroyed due to corrosion effect. This process is limited by diffusion, because the reagent ( $O_2$ ,  $H_2$ ) transport to the reaction zone is accomplished by diffusion.

The known attempts to describe the effects of cold-deformation on solubility and diffusivity of interstitial impurities, based on the influence of dislocations decorated by the Cottrell type segregations had no unequivocal results. This is mainly due to insufficient capture ability and high diffusion conductivity of the near-dislocation segregation regions [5, 12, 13]. in the Cottrell Cloud Model.

To sum up, the Cottrell Cloud Model is a qualitative model and consequently some aspects of the yield point phenomena are not explained. Thus for quantitative description of the phenomena it will be useful to take into account the phase segregation along dislocations. In the present work analysis has been made on the possibility of interpretation of these effects. This analysis is based on the further development of the theory, of the influence of the near-dislocation segregation regions, on impurity diffusion and solubility, and the existence

of different types of the segregations on dislocations. The present paper has also taken into account the results [17], on the interpretation of the anomalies of transition impurity diffusion in Al-crystals with high dislocation density.

The major components of this work could be outlined as follows:-

1. The analysis of experimental data on the interstitial impurity diffusion in non-deformed crystals (with low dislocation density) by Zener Model. This gives the normal diffusion which will be used as a standard for comparison purposes.
2. Critical analysis of experimental data on the interstitial impurity diffusion and solubility in cold-worked crystals (with high dislocation density) and weak aspects of known interpretations. This gives anomalous diffusion.
3. Development of the Model.
4. Thermodynamic and crystallographic analysis of the model.

## CHAPTER I

### THE CONSIDERATION OF THEORETICAL AND EXPERIMENTAL DATA ON THE DIFFUSION OF INTERSTITIAL IMPURITIES IN NON-DEFORMED BCC AND FCC METALS

1.1 The mechanism of diffusion has already been studied in detail [19-23]. As is well known, the problem can be reduced to that of a small atom moving at random in successive interstitial positions.

Quantitative measurements of the rate at which a diffusion process occurs are usually expressed in terms of the diffusion coefficient, the activation energy and the entropy or frequency factor, which are known as the diffusion characteristics. Since diffusion occurs as a result of the random motion of particles which are always thermally activated in solids, the diffusion coefficient thus becomes a very strong function of temperature (T) and the relation of the type

$$D = D_0 \exp \{-Q/RT\} \quad (1.1)$$

is often followed.

Where: Q is the activation energy;  $D_0$  is the frequency factor; R is the gas constant and T is the temperature in K.

Different attempts have been made to evaluate the diffusion characteristics, namely Q and  $D_0$ , of interstitial impurity diffusion in non-deformed BCC and FCC metals. In this Chapter the writer has considered the validity of Zener theory [18] and the "Random Walk"

theory [24] by some experimental results on  $D_0$  and  $Q$  and the "Quantum Nature of Hydrogen Impurity" [12,25, 26]. Here dilute solutions are considered.

### 1.2 HYPOTHESIS FOR THE EVALUATION OF THE ACTIVATION ENERGY 'Q' BY THE ZENER MODEL:

According to [18] the activation energy can be calculated on the basis of the distortion induced by the interstitial atom around the positions  $(\frac{1}{2}00)$  of the matrix lattice and from the hypothesis that the activation energy is mainly a strain energy of the lattice, which has already been proposed by Zener.

With reference to Figs. (1) and (2), [18] it can be seen that, if the height of the interstitial cavity adjacent to an occupied one is increased until it has reached a value equal to the diameter of the interstitial atom, the potential barrier between the two positions goes to zero and the interstitial atom can pass from one position to the other. Hence the activation energy of interstitial diffusion can simply assumed to be the strain energy required to obtain, the next to the occupied cavity, of equal size, in which the interstitial atom can be obtained.

#### 1.2.1 CALCULATION OF THE ACTIVATION ENERGY

As in many similar cases, calculation of the displacements, and hence of the activation energy, can be made with sufficient approximation using the theory of elasticity [18].

A qualitative scheme of the displacements of the atoms of the matrix around and occupied interstitial cavity is represented in Fig. (2), [18]. Taking into account the very low height of the cavity itself, to enlarge the same to the size of the interstitial atom, it is sufficient to pull apart the two atoms A and B along the Z-axis. The displacement of the centers of these two atoms will be simply given by Vegards law. Therefore the displacement of these two points is equal:  $(d-h)/2$  and the mean deformation of the unit cell between points A and B will be:

$$\epsilon_0 = \frac{(d-h)}{a} \quad (1.2)$$

Where:  $d$  is the diameter of the interstitial atom,  $a$  is the lattice parameter and  $h$  is the height of the interstitial cavity.

To calculate the strain energy in the interior of the sphere as a first approximation one may simply take the uniform mean strain given by Eqn. (1.2). For the part external to the sphere in polar coordinates  $r, \psi, \theta$  and for a typical value of Poisson modulus of  $1/3$  the strain distribution thus deduced as in [18]..

$$\begin{aligned} \epsilon_r &= \frac{-B}{r^3} (0.33 \sin^2 \psi + \cos^2 \psi) \\ \epsilon_\psi &= \frac{-B}{r^3} (0.11 \sin^2 \psi + 0.28 + 0.11 \cos^2 \psi) \\ \gamma_{r\psi} &= \frac{-B}{r^3} (0.89 \sin \psi \cos \psi) \\ \epsilon_\theta &= \frac{B}{r^3} (0.11 \sin^2 \psi - 0.28 + 0.78 \cos^2 \psi) \end{aligned} \quad (1.3)$$

Where:  $\epsilon_r$ ,  $\epsilon_\psi$  and  $\epsilon_\theta$  are the normal components of strain and  $\gamma_{r\psi}$  the shear strain. The two other components of shear  $\gamma_{r\theta}$  and  $\gamma_{\psi\theta}$  vanish for reasons of symmetry. The constant B is equal to:

$$\theta = \frac{\epsilon_a a^3}{8} \quad (1.4)$$

Where,  $\epsilon_a$  is the strain for  $r = a/2$  and  $\psi = 0$  and it is simply given by:-

$$\epsilon_a = \frac{2(d-h)}{a} \quad (1.5)$$

The strain energy is calculated as the sum of the two separate parts: the energy external to the sphere of radius  $a/2$  and the energy of the sphere having radius  $a/2$  with the interstitial position at its center.

Writing the strain energy per unit volume in the form [31].

$$W = G(\epsilon_r^2 + \epsilon_\psi^2 + \epsilon_\theta^2 + \frac{1}{2} \gamma_{r\psi}^2) + \frac{3\nu^*}{2(1+\nu^*)\chi} (\epsilon_r + \epsilon_\psi + \epsilon_\theta)^2 \quad (1.6)$$

Where: G is the shear modulus;  $\chi$  is the compressibility and  $\nu^*$  is the Poisson ratio, from Eqn.(1.3) and Eqn.(1.2) by integrating over the volume, the energy W associated with the enlargement of the interstitial cavity is obtained [18].

$$W = \left( \frac{1.52\pi}{6} + \frac{\pi}{6} \right) [aG(d-h)^2] \quad (1.7)$$

With reference to Fig. (2) in Eqn. (1.7), the second term representing the strain energy of the interior of the sphere of radius  $a/2$  corresponds mainly to the work done by the attractive force between atoms A and B. From Eqn. (1.7) referring to N atoms per mole, the activation energy is immediately obtained as [18].

$$Q = 1.3NGa(d-h)^2 \left(1 - \frac{\beta Q}{RT_m}\right)$$
$$Q = \frac{1.3NGa(d-h)^2 RT_m}{RT_m + 1.3NGa(d-h)^2 \beta} \quad (1.8)$$

Where: G is the elastic constant  $\approx 10^{11} \text{N/m}^2$

$$\beta = \frac{T_m}{G_0} \left(\frac{dG}{dT}\right) \approx (0.25 - 0.45)$$

$T_m$  :melting temperature

R :the gas constant.

### 1.2.2 COMPARISON OF THE THEORETICAL AND EXPERIMENTAL VALUES OF ACTIVATION ENERGIES:

The values of the activation energies calculated according to Eqn.(1.8)(for solid solutions) are given in table - I [18] in comparison with the experimental values.

As may be seen, the agreement between the theoretical values and the experimental ones may be considered satisfactory. In any case, all results clearly confirm that at least the greater part of the activation energy for interstitial diffusion may be simply interpreted as a distortion energy of the matrix lattice.

### 1.3 EVALUATION OF THE FREQUENCY FACTOR ' $D_0$ ' BY ZENER MODEL

From the theory of Wert and Zener [19,21] (within the "Random Theory"),  $D_0$  is given by:

$$D_0 = \frac{1}{6} \nu a^2 \exp \frac{\Delta s}{R} \quad (1.9)$$

Where:  $a$  is the lattice parameter,  $\nu$  is the lattice vibration frequency,  $\Delta s$  is the entropy of activation and  $R$  is the gas constant.

In this theory the entropy of activation is simply related to the coefficient  $\beta/T_m$  of decrease of elastic moduli with temperature by the equation:

$$\Delta s = \frac{\beta Q}{T_m} \quad (1.10)$$

$Q$  is the activation energy and  $T_m$  is the melting temperature of the metal.

The fact that the activation energy can actually be calculated as elastic strain energy stored in a thermal fluctuation around an interstitial position confirms the validity of Zener's model.

The frequency,  $\nu$ , on which the diffusion process depends has been evaluated by Zener [19,21] under the hypothesis that the interstitial atom oscillates in a sinusoidal potential of path equal to the distance between two interstitial positions. Hence we have:

$$v = \left( \frac{2Q}{a^2 m} \right)^{\frac{1}{2}} \quad (1.11)$$

Where:  $m$  is the mass of the interstitial atom and

( $v$ -Debye frequency =  $5 \times 10^{12}$  Hertz)

The theoretical values of  $D_0$  calculated with Eqns. (1.9) and (1.10) using the lattice frequency are given in table-I, together with the experimental results. The agreement between the two groups of values can be considered satisfactory, as the experimental results are in good agreement with the Zener model.

In the work of D. Bergner [24], analogous analysis of the experimental data has been done, on the diffusion parameters  $D_0$  and  $Q$  for the interstitial solutes such as: O, N and C in Ag, Cu,  $\gamma$ -Fe, Ni, Pt,  $\alpha$ -Th, and Co (non-deformed FCC-metals); C, N and O in  $\beta$ -Ti,  $\beta$ -Zr,  $\beta$ -Hf, V, Nb, Ta, Cr, Mo and W (non-deformed BCC-metals), obtained by using different methods, which are grouped into two, consisting of different techniques as in table - II.

In [24] it has been shown that there is a satisfactory agreement of the experimental results with the Zener model. The experimentally obtained values of  $\beta$ , Eqn. (1.8) : in all BCC-metals (except O in Cr and W which is negative),  $\beta = 0.27 \pm 0.07$  in all FCC-metals,  $\beta = 0.34 \pm 0.10$ . These are approximately, within the limit

Table-I Theoretical and Experimental Activation Energies (Q)  
and Frequency Factors ( $D_0$ ) Values

System	d, Å	h, Å	a, Å	$\frac{(d-h)}{a}$	Q, KJ/mol		$D_0$ , cm <sup>2</sup> /s		References
					Theor.	Exp.	Theor.	Exp.	
H in $\alpha$ -Fe	0.60	0.38	2.86	0.077	5	13	-	-	[77-79]
C in $\alpha$ -Fe	1.54	0.38	2.86	0.406	11	84	0.011	0.020	[23]
N in $\alpha$ -Fe	1.42	0.38	2.86	0.364	92	76	0.008	0.003	[23]
C in Ta	1.54	0.44	3.30	0.330	176	166	0.009	0.016	[34,80]
N in Ta	1.42	0.44	3.30	0.297	146	157	0.008	0.006	[26,34]

Table II. Essential Methods for Measuring the Diffusion Parameters. [81,82].

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Group-I Macroscopic (mass-flow) methods	Group-II Relaxation methods (on an atomic scale)
1- Tracer sectioning technique	1- Snoek - Effect: Internal friction
2- Sandwich - methods	2- Elastic After Effect
i) Serial sectioning and chemical analysis	3- Quasielastic scattering of neutrons
ii) Microprobe analysis on a metallographic section.	4- Mössbauer Effect.
3- Steady state permeation of gaseous diffusant under a pressure gradient	
4- Outgassing: Time dependence of the amount of material evolved.	
5- Gorsky-Effect: Time dependence of redistribution of solute in an inhomogeneously stressed body	

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of experimental error, in agreement with the value of  $\beta=0.24$  estimated on the basis of the Gruneisen model of anharmonicity, Keyes [27].

The diffusion mechanism of the light interstitial solute, namely hydrogen in non-deformed FCC and BCC metals, can also be studied satisfactorily by the quantum nature of the hydrogen impurity which is a more general approach. This is considered in the next section.

#### 1.4 THE QUANTUM NATURE OF HYDROGEN IMPURITIES:

Other than the theory of elasticity the quantum nature of impurities is crucial for hydrogen. Detail investigations on localization phenomena and diffusion mechanisms of the interstitial solutes in non-deformed BCC and FCC metals are considered [28].

Experimentally, the location of hydrogen in BCC metals is investigated by ion-channeling techniques [28]. The results indicate both tetrahedral and octahedral occupancy as shown in Figs. (3) and (4) depending on the host metal in question. In Nb, Ta and V the assignment is the tetrahedral sites, where as in Cr, which has a relatively small lattice constant, the octahedral location is found to be more probable.

The neutron diffraction studies [66-70] indicate that hydrogen occupies the tetrahedral sites in BCC metals.

The localized state for the tetrahedral site was searched for by requiring that the wave function is localized in a cube with its center at the tetrahedral site and its corners at the nearest atoms or octahedral points. With these boundary conditions the localization to the tetrahedral interstice does not occur for any of the FCC metals studied, as indicated by the energy of localization (self-energy trapping) [25].

The activation energy,  $Q$ , for hydrogen in non-deformed BCC metals [25] is (1-2) KJ/mol, which is less than the experimental value (4.8-9.6) KJ/mol. [29]. The smallness of the calculated value is mainly due to the underestimation of the short range orthogonality repulsion experienced by hydrogen near the host-metal nuclei [30].

In [29] the measured temperature independent pre-factor of the diffusion constant in BCC metals does not show the  $1/\sqrt{M}$  dependence on the isotope mass  $M$ , as classical oscillator model predicts. This is an indication that the potential for hydrogen is indeed strongly unharmonic [25].

Diffusion model for hydrogen in FCC metals is totally different from the one described for BCC metals. First, it is noted that in the high temperature region, the diffusion activation energy in FCC metals is typically (19-39) KJ/mol [29], which is much more than the

calculated localization energies in the octahedral sites. On the other hand, according to the calculations, localization in the tetrahedral site is improbable and thus hydrogen would not be localized at the tetrahedral site during the activation process, but its wave function should be spread over several interstices. According to the experiments [25], the temperature independent prefactor of the diffusion constant for H, D and T (hydrogen isotopes) behaves as the harmonic oscillator predicts, i.e. the ratio of the factors is  $1:\sqrt{2}:\sqrt{3}$  [41].

The known experimental data on the diffusion parameters of the interstitial impurities in non-deformed crystals (FCC and BCC metals) are consistent with the Zener model. The main contribution to the diffusion parameters is due to the elastic interaction of interstitial impurities with the matrix atoms. Hence it follows that the interstitial impurities could interact strongly with local elastic fields in the near-dislocation regions. In other words the near-dislocation regions could influence the diffusion and solubility of the interstitial impurities especially in deformed crystals containing high dislocation density. To study this effect the diffusion (and solubility) parameters of non-deformed crystals with negligible dislocation density will be taken as a standard level, i.e. "normal" diffusion (and normal solubility) for comparison. This effect will be considered in the next Chapter.

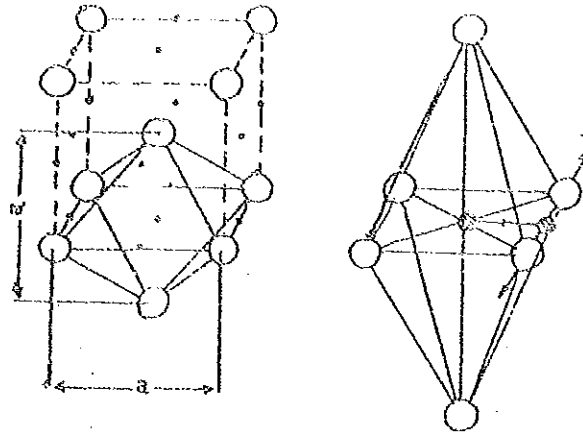


Fig. 1: Positions of the interstitial atom in BCC lattice and scheme of diffusion mechanism. In the figure on the left the points represent the possible positions of the interstitial atoms.

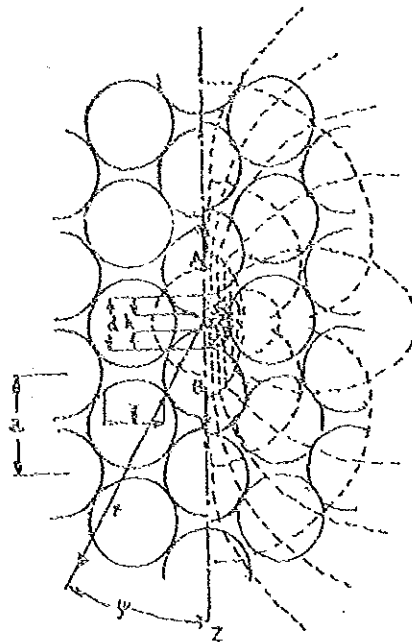
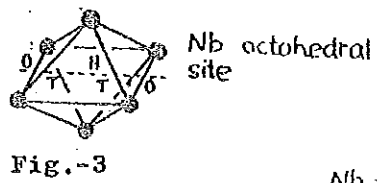


Fig. 2: Qualitative scheme of the distortion of BCC network around an interstitial atom. The lattice is sectioned on a (110) plane: on the left the undistorted lattice is sketched for comparison. The dotted lines correspond to the principal stresses in the equivalent continuous solid.



Nb tetrahedral site

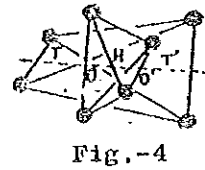


Fig.-3: Self-trapping of hydrogen impurity into the Octahedral Site in Nb.

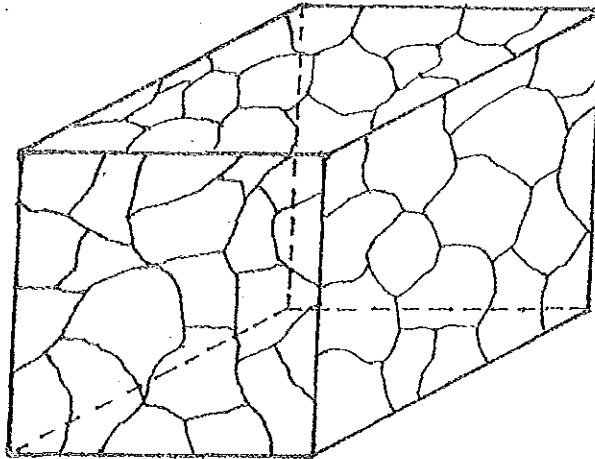
Fig.-4: Self-trapping of Hydrogen into the Tetrahedral Site in Nb.

## CHAPTER II

### ANALYSIS OF EXPERIMENTAL DATA AND KNOWN INTERPRETATIONS OF THE INFLUENCE OF COLD- DEFORMATION ON DIFFUSION AND SOLUBILITY OF INTERSTITIAL IMPURITIES IN METALS

#### 2.1 DISLOCATIONS IN COLD-DEFORMED CRYSTALS:

Dislocations constitute the so-called line of defects of a crystal. The displacement of the lattice required to produce a dislocation results in an elastic field created around the dislocation. A dislocation line is continuous. It can never end within an otherwise perfect region of the crystal, but must terminate at a free surface, another dislocation line, a grain boundary or some other defect. This is illustrated in Fig. (5). The existence of dislocation permits metals to be plastically deformed with ease, a circumstance upon which our modern technology is so dependent.



(Fig. 5)

Dislocations have both macroscopic (length) and microscopic (cross-sectional) properties.

### 2.1.1 MACROSCOPIC ASPECT

Dislocation density ( $\rho_d$ ) is defined as the total length of dislocations ( $l$ ) per unit volume. That is,  $\rho_d = l/v$ , normally quoted in units of  $\text{cm}^{-2}$ . It is observed that,

$$\begin{aligned} \rho_d &\lesssim 10^{11} \text{ cm}^{-2} \\ \text{ie } \rho_d &\approx 10^{11} \text{ cm/cm}^3 = 10^6 \text{ km/cm}^3 \\ &\sim 100 \text{ (Earth's diameter)/cm}^3 \end{aligned}$$

### 2.1.2 MICROSCOPIC ASPECT

From the consideration of the local elastic field near-dislocation region, the cross-sectional diameter of the dislocation pipe ( $d_d$ ) is estimated to be:

$$d_d \lesssim 100\text{\AA}.$$

The atomic fraction (lattice atoms and impurity atoms) in the trap region, namely the dislocation region ( $N_d$ ), could be expressed as

$$N_d \approx \alpha \rho_d b^2 \quad (2.1)$$

Where:-  $b$  is the atomic spacing ( $\sim 3\text{\AA}$ ),  $\alpha$  is the number of atoms in the cross-section of the dislocation pipe.

$$(\alpha \approx d_d^2/b^2 \lesssim 10^3)$$

$$\text{Thus: } N_d \lesssim 10^{-1}$$

### 2.1.3 INFLUENCE OF DISLOCATION ON THE SOLUBILITY OF INTERSTITIAL IMPURITIES IN DEFORMED CRYSTALS

The solubility of the interstitial impurities is mainly influenced by the trap-effect due to dislocation. The contribution to the total solubility of interstitial

impurities in the matrix due to this effect, could be estimated as:-

$$N(\text{imp})_L \approx C_L N_L \lesssim 10^{-2} \quad (2.2)$$

Where:-  $C_L$  is the local impurity concentration in the near-dislocation region ( $C_L \lesssim 10^{-1}$ ), which is usually much larger than the impurity concentration in the normal lattice ( $C_L \gg C$ ).

#### 2.1.4 INFLUENCE OF DISLOCATION ON THE DIFFUSION OF INTERSTITIAL IMPURITIES IN DEFORMED CRYSTALS

The local diffusion coefficient of interstitial impurities along the near-dislocation regions ( $D_L$ ), could be:  $D_L \gg D$ ,  $D$  being the impurity diffusion coefficient in the normal matrix.

In the case of  $D_L \gg D$ , the considerable contribution in the impurity diffusion could be accounted for the so-called diffusion by dislocation effect (the enhancement of diffusion). In the case of  $D_L < D$ , the contribution could be accounted for the trap-effect by dislocation (the diminution of diffusion). Detailed discussion of these effects will be considered in sections (2.2), (2.3), (2.4) and chapter-3.

#### 2.2 ANALYSIS OF EXPERIMENTAL DATA ON ANOMALOUS DIFFUSION OF THE IMPURITIES IN COLD-DEFORMED METALS

There are a large number of experimental works devoted to the study of the influence of prior cold-deformation on diffusion and solubility of interstitial

impurities in metals. Some of them are considered in [5, 12, 13, 32].

For instance, in the works [33-37] it has been shown that prior cold-plastic deformation slows down the diffusion of C in Fe, Ni, Fe-Si (3.4 wt%) and Fe-Cr (2 wt%) alloys at low temperatures that could be due to the defect content, particularly that of dislocation density in the specimens. As shown in [18,38,39], the diffusion mobility of C, N and H atoms in deformed metals, such as Fe diminish as the structural imperfection increases. According to the data [40,41] prior cold plastic deformation, causes a considerable diminution in diffusion and increase in solubility of hydrogen impurity in Fe and Fe-based alloys. This is accompanied with the increase in dislocation density in the specimens. It is also emphasized in [18,33-41] that the activation energies of the impurity diffusion in cold-worked specimens are considerably higher than those in non-deformed ones. The analogous regularities have been established in [42-44], during studying the influence of cold-plastic deformation on diffusion of nitrogen and oxygen in Nb and Nb-based alloys.

In [26,45-47], it has been shown that structural defects, produced during prior deformation of specimens, diminish the diffusion of N and H, and raise the impurity solubility in an analogous manner, structural defects have influence on the diffusion and solubility of H in deformed Ni [48].

Some information about the diminishing of hydrogen diffusion and increasing of its solubility in cold-worked metals and alloys is contained in works [1,49-62].

In some works [32], it has been found out that cold-deformation causes dissolving of intermetallic particles of carbides and nitrides in steels ie. the deformation increases the effective solubility of the impurities.

In a more detailed form, the experimental data quoted above, could be formulated as follows:-

1. The diffusion of some interstitial impurities ( $D_\epsilon$ ) in cold-deformed metals and alloys at low temperatures in many cases are less (by 1-2 orders) than the impurity diffusion coefficient ( $D$ ) in non-deformed specimens at the same temperature (Table-III). The magnitude of the ratio,  $D_\epsilon/D$ , depends on the degree of plastic deformation ( $\epsilon$ ), of the specimens and on the temperature ( $T$ ) of the diffusion annealing which is much lower than the recrystallization temperature.
2. The temperature dependence of  $D_\epsilon$  and  $D$ , in a satisfactory approximation, can be described by the Arrhenius type equations. That is:-

$$D_{\epsilon} \approx D_{oe} \exp \{-Q_{\epsilon}/RT\}, \quad (2.3)$$

$$D \approx D_o \exp \{-Q/RT\}, \quad (2.4)$$

$$Q_{\epsilon} \approx Q + \Delta H \quad (2.5)$$

Where:-  $Q_{\epsilon}$  is the activation energy of the impurity diffusion in deformed specimens;  $Q$  is the activation energy of the impurity diffusion in non-deformed specimens containing negligible concentration of structural defects;  $\Delta H$  is change in enthalpy of a system, which is about (15-60) KJ/mol. (table-III);  $D_{oe}$  and  $D_o$  are the frequency factors of the impurity diffusion coefficients in deformed and non-deformed specimens respectively;  $R$  is the gas constant and  $T$  is temperature.

3. The magnitude of the ratio  $D_{oe}/D_o$ , is usually much larger than 1. In many cases, it decreases with the increase in the degree of deformation of specimens and could be represented as follows:-

$$\frac{D_{oe}}{D_o} \approx \frac{1}{\gamma_o(\epsilon)} \quad (2.6)$$

Where:-  $\gamma_o(\epsilon)$  characterizes the imperfection content in deformed specimens at a given value of  $\epsilon$  (deformation), in all cases  $\gamma_o(\epsilon) \ll 1$ . From Eqns. (2.3) - (2.6) and the very fact that  $D_{\epsilon} = D$  for  $\gamma_o = 0$ , it follows:-

$$\frac{D_{\epsilon}}{D} = \frac{1}{1 + \gamma_o(\epsilon) \exp \{\Delta H/RT\}} \quad (2.7)$$

$$\left(\frac{D}{D_\epsilon} - 1\right) \approx \gamma_0(\epsilon) \exp[\Delta H/RT] ,$$

$$\left(\frac{D}{D_\epsilon} - 1\right) \approx \gamma(\epsilon) , \quad (2.8)$$

For cold-worked Fe[35]:

$$\rho_d(\epsilon) = (0.54)10^{11} \sqrt{\epsilon} , \quad (2.9)$$

$$\text{then } \gamma(\epsilon) \sim \rho_d(\epsilon) , \quad (2.10)$$

where:-  $\rho_d$  is the dislocation density and  $\epsilon$  is deformation in %.

The dependence of  $\left(\frac{D}{D_\epsilon} - 1\right)$  on  $\rho_d(\epsilon)$ , for C in Fe, is shown in Fig. -(6), based on the data in table-III.

From Eqn. (2.1):-

$$\gamma_0(\epsilon) \approx N_d , \quad (2.11)$$

This will be verified by the theoretical consideration in section (2.3).

4. From experimental data [50,51] on the total content ( $C_\epsilon$ ) of the interstitial impurity (hydrogen) in deformed specimens (steels) and data [63] on the equilibrium concentration (C) of the impurity in non-deformed specimens, the expression in [5] follows:-

$$\frac{C_\epsilon}{C} \approx 1 + \gamma_0(\epsilon) \exp[\Delta H/RT] , \quad (2.12)$$

$$\frac{C_\epsilon}{C} \gg 1$$

Where:-  $\Delta H$  and  $\gamma_0(\epsilon)$  are the same quantities as in Eqns. (2.5) and (2.6).

Similar relationships could be formulated for the other interstitial impurities [32]. These empirical relations are illustrated by the analysis of some experimental works, whose results are represented in table-III.

5. From the experimental results on the diminution of impurity diffusion, it follows that the diffusion by dislocation ( $D_d$ ) is negligible in comparison to the impurity diffusion in matrix and the diffusion with trapping-effect.

The parameters,  $\alpha_d$ ,  $\Delta H_d$  and  $D_d$  are the characteristics of the near-dislocation regions. It will be shown that in the theoretical considerations the parameters  $\alpha_d$ ,  $\Delta H_d$  and  $D_d$  characterize the near-dislocation segregation regions. In other words they contain some information on the structure of the segregation regions. On the basis of this information a suitable segregation model will be discussed in chapters 3 and 4.

### 2.3 ANALYSIS OF THE KNOWN (INTERPRETATIONS) MODELS

There have been many works devoted to the study of the diminution of the interstitial impurity diffusion, and in particular, the anomalous high values of  $Q_e$  and  $D_{oe}$ , and the increase of the impurity solubility in cold-worked metals and alloys.

The nature of traps in metals and alloys (steels) are classified in [64,65].

Table- III. Results of the Analysis of Some Known Experimental Data on Impurity Diffusion and Solubility in Deformed Metals by Using Eqns. (2.1) (2.13) [2, 5, 35, 37, 48]

System (C <sub>1</sub> in atomic fraction)	T, K	Z, %	$\rho$ cm <sup>-2</sup>	Q, KJ/mol D <sub>0</sub> , cm <sup>2</sup> /s	D <sub>z</sub> /D At given T	$\Delta H_z$ , KJ/mol.	$Y_0$ cm <sup>-2</sup>	$\alpha_z^*$ (z=0)	** [C <sub>1</sub> ], Atomic Fraction
C <sub>1</sub> /Fe - Fe {10 <sup>-4</sup> - 10 <sup>-5</sup> }	(523-773)	75	= 10 <sup>11</sup>	90 6 x 10 <sup>-2</sup>	1x10 <sup>-2</sup> 523°K	58±5	2x10 <sup>-4</sup>	= 10	[1 - 10 <sup>-1</sup> ]
C/Fe-3.5 wt% S <sub>1</sub> {10 <sup>-4</sup> - 10 <sup>-5</sup> }	(523-1023)	75	= 10 <sup>11</sup>	74 4x10 <sup>-3</sup>	9x10 <sup>-2</sup> 523°K	25±3	3x10 <sup>-2</sup>	= 10 <sup>2</sup>	[10 <sup>-2</sup> - 10 <sup>-3</sup> ]
H <sub>2</sub> /Fe -0.18(C {6 x 10 <sup>-4</sup> }	(523-523)	50	= 10 <sup>11</sup>	8 8x10 <sup>-4</sup>	1.4x10 <sup>-2</sup> 523°K	32±3	3x10 <sup>-2</sup>	= 10 <sup>3</sup>	[2 x 10 <sup>-2</sup> ]
D <sub>2</sub> /N <sub>1</sub> {10 <sup>-4</sup> - 10 <sup>-5</sup> }	(418-502)	98	= 10 <sup>11</sup>	40 5x10 <sup>-3</sup>	5x10 <sup>-1</sup> 218°K	17±2	6x10 <sup>-3</sup>	= 10 <sup>2</sup>	[10 <sup>-2</sup> - 10 <sup>-3</sup> ]

\*: The values of  $\alpha_z$  have been obtained by:  $\alpha_z = \frac{Y_0 b}{D_z \rho_z}$  (2.13)

\*\* From Eqn. (2.2),  $C_1 = C_E/Y_0$

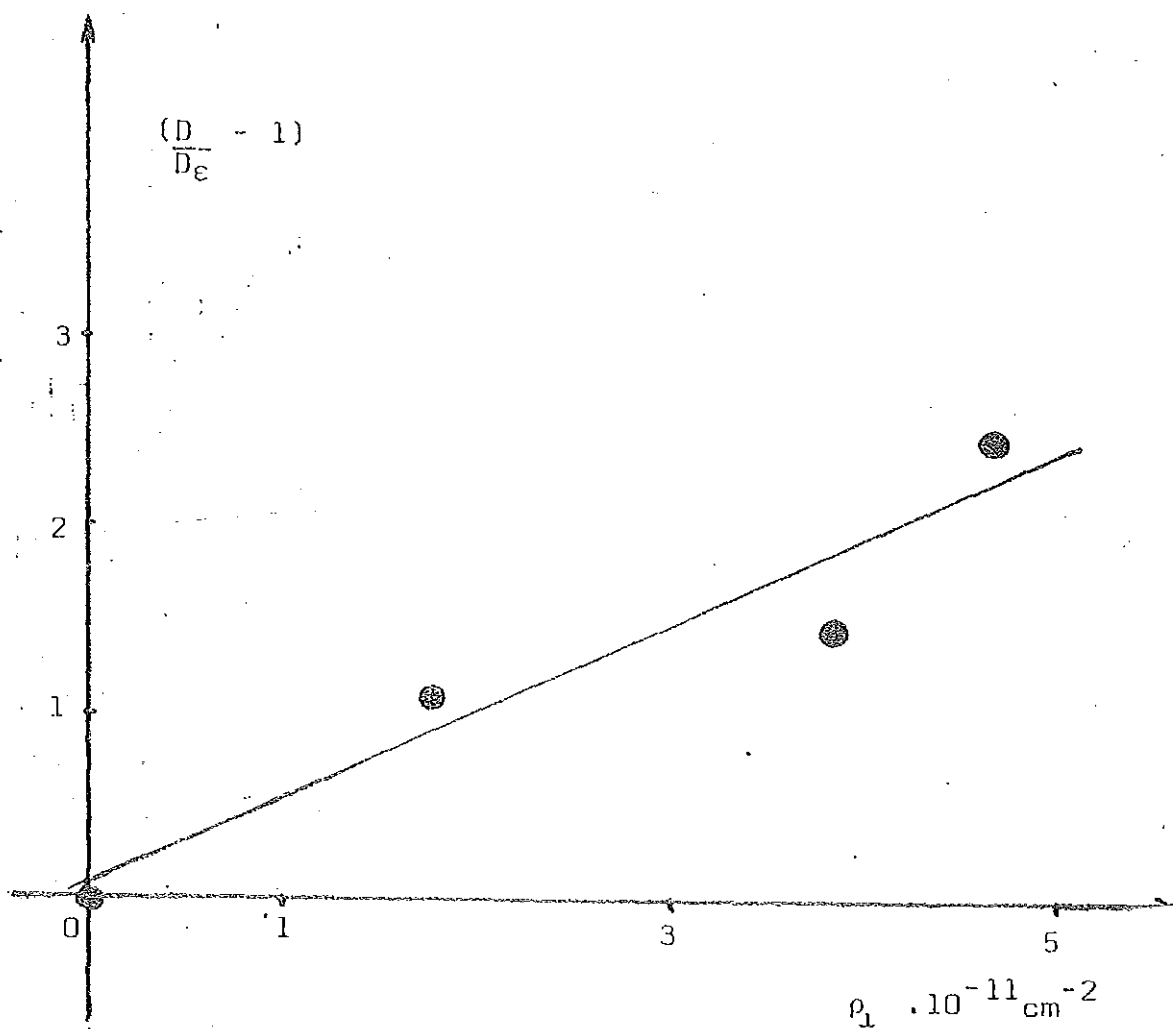


Fig. 6: Graph of the dependence of  $\left(\frac{D}{D\epsilon} - 1\right)$  on  $\rho_{\perp} (\epsilon)$ . (● = Experimental)

Darken and Smith [1] probably first suggested that the diffusion of an interstitial impurity (hydrogen) in a cold-worked steel is impeded by lattice imperfections.

Mc. Nabb and Foster [4] developed a general formulation for the diffusion of interstitial impurity (hydrogen) in metals and alloys (steels) with the so-called reversible traps. Oriani [5] gave a thermodynamic interpretation to Mc Nabb and Fosters theory, again confining considerations to reversible impurity traps, based on the assumption that interstitial atoms upon normal lattice sites and captured in traps are in local thermodynamic equilibrium.

Recently Sakamoto [13] has carried out an analysis of the apparent diffusivity of impurity (hydrogen) based on the hypothesis that states:-

1. There exists a local equilibrium between the trap regions (the near-dislocation segregation regions) and the matrix solution.
2. The distribution law for the impurity corresponds to the linear concentration dependence.

The author has obtained different equations with regard to different trap models. These equations are so complicated that they could not be used for describing experimental data. As an illustration, the simplest equation of all, derived with regard to the "two-energy-level" trap model, is indicated below.

$$\begin{aligned}
 D_a = & \frac{D_\ell^0 \exp\left(-\frac{E_\ell}{RT}\right)}{1-f_t \left\{1-\exp\left(-\frac{\Delta\bar{G}_{t,\ell}}{RT}\right)\right\}} \left[1-f_t - f_t(1-f_{tx})\right] \\
 & \times \left\{1 - \frac{D_k^0}{D_\ell^0} \exp\left(-\frac{E_k-E_\ell}{RT}\right)\right\} \\
 & + f_t \exp\left(-\frac{\Delta\bar{G}_{t,\ell}}{RT}\right) \left\{(1-f_{tx}) \frac{D_p^0}{D_\ell^0} \exp\left(-\frac{E_p-E_\ell}{RT}\right)\right. \\
 & \left.+ f_{tx} \frac{D_d^0}{D_\ell^0} \exp\left(-\frac{E_d-E_\ell}{RT}\right)\right\} \quad , \quad (2.14)
 \end{aligned}$$

Where:-  $\ell, k, p$  and  $d$  are the impurity jump rates;  $D_\ell, D_k, D_p$  and  $D_d$  are the effective diffusivities;  $E_\ell, E_k, E_p$  and  $E_d$  are the corresponding activation energies, with regard to the jumping processes of  $\ell \leftrightarrow \ell, \ell \rightarrow t, \ell \leftarrow t$  and  $t \leftrightarrow t$  intersites respectively;  $\ell$  being the lattice sites and  $t$  the trap sites;  $f_\ell$  is fraction of normal lattice sites,  $f_t$  is fraction of trapping sites and  $f_\ell + f_t = 1$ .

$f_{tx}$  is fraction of  $n_t$  sites from which impurity can jump with jump rate  $d$  in the individual trap cluster,  $n_t$  being the number of trap sites per unit volume.

In this work the following assumptions have been considered.

1. The fraction of the trap regions is negligible i.e.

$$f_t \ll 1$$

2. The boundary zones between the trap regions and the normal lattice is of negligible thickness such that:-

$$f_{tx} \approx 1$$

$$\text{i.e. } (1-f_{tx}) \approx 0$$

Then Eqn. (2.14) can be reduced to

$$D_a \approx \frac{D_\ell^0 \exp[-E_\ell/RT]}{1 + f_t \exp[-\frac{\Delta\bar{G}^{\bar{t},\ell}}{RT}]} \times [1 + f_t \exp(-\frac{\Delta\bar{G}^{\bar{t},\ell}}{RT}) \frac{D_d^0}{D_\ell^0} \exp(-\frac{E_d - E_\ell}{RT})] \quad (2.15)$$

Using the notations as in this work, it follows:-

$$D_a = D_{\text{eff}}, \quad f_t = N_L$$

$$D_\ell^0 = D_o, \quad E_\ell = Q$$

$$\exp(-\frac{\Delta\bar{G}^{\bar{t},\ell}}{RT}) = K_L,$$

$$D_d^0 = D_{oL} \quad \text{and} \quad E_d = Q_L$$

$$\text{Then: } D_{\text{eff}} \approx \frac{D}{1 + N_L K_L} \left[ 1 + \frac{N_L K_L D_L}{D} \right], \quad (2.16)$$

Where:- the first term,  $\frac{D}{1 + N_L K_L}$ , corresponds to diffusion with-trapping-effect, and the second term,  $\frac{D_L N_L K_L}{1 + N_L K_L}$ , corresponds to transport-by-dislocations effect.  $D_L$  is the diffusion coefficient of an impurity in segregation regions along dislocations,

$$\text{ie. } D_L = D_{oL} \exp(-Q_L/RT), \quad (2.17)$$

$K_L$  is the equilibrium constant of impurity distribution between the trap regions and the normal lattice

$$\text{ie. } K_L = \exp(-\frac{\Delta S_L}{R}) \exp(\frac{\Delta H_L}{RT}), \quad (2.18)$$

$\Delta H_L$  and  $\Delta S_L$  being the standard enthalpy and entropy changes of the system when one mole of the impurity atoms passes from the trap regions into the normal lattice.

Sakamoto [13], used a model of saturated trap regions in order to reduce Eqn (2.14) to Eqn (2.7), which corresponds to the experimental results (table-III). In this approximation, Sakamoto has neglected the transport-by-dislocation effect in Eqns. (2.14) and (2.16), (since in saturated trap regions,  $\nabla C_L = 0$ ) and obtained:

$$D_{\text{eff}} \approx \frac{D}{1+N_L K_L} \quad (2.19)$$

Oriani [5] and Leblond and Dubois [71] have obtained the same expression as Eqn. (2.19) without taking into account any physical approximation. In other words, they neglected the impurity transport-by-dislocations, giving no explanation.

It is possible to show that within the approximation of the saturated trap regions, the distribution constant ( $K_L$ ) is also zero besides to  $\nabla C_L = 0$ . This could be illustrated as follows.

Let  $\theta_L$  and  $\theta_L$  be the fraction of the available sites in the normal lattice and trap regions respectively, occupied by impurity atoms such that:

$$\theta_L = \frac{C_L}{C_{L(\text{max})}} \quad , \quad \theta_L = \frac{C_L}{C_{L(\text{max})}} = \frac{C}{C_{(\text{max})}} \quad (2.20)$$

Where:-  $C_{L(\text{max})} = \text{const.}$  and  $C_{L(\text{max})} = \text{const.}$  are the maximum possible local concentrations of the impurity atoms in the trap regions and the normal lattice respectively.

Then the distribution law describing the saturation property could be expressed as [5].

$$K_L = \left\{ \frac{\theta_L}{(1-\theta_L)} \right\} / \left\{ \frac{\theta_L}{(1-\theta_L)} \right\}, \quad (2.21)$$

For a dilute matrix solution,  $C_L \ll 1$ , i.e.  $\theta_L \ll 1$ .

Thus Eqn. (2.21) gives:

$$K_L \approx \frac{1}{\theta_L} \left( \frac{\theta_L}{1-\theta_L} \right),$$

$$\theta_L \approx \frac{K_L \theta_L}{1+K_L \theta_L}, \quad (2.22)$$

From Eqn. (2.22), it follows that there are two limiting cases (approximations).

1. The non-saturated case, corresponding to the linear concentration dependence, which is realized

when  $K_L \theta_L \ll 1$ .

$$\text{i.e. } \theta_L \approx K_L \theta_L, \quad (2.23(a))$$

$$\text{and } C_L \approx K_L^* C_L, \quad \frac{\partial C_L}{\partial C_L} = K_L^*, \quad (2.23(b))$$

where:  $C_L = C$  and  $C_L$  are the impurity concentrations in the normal lattice and trap regions, and  $K_L^* = \frac{C_L(\max)}{C_L(\max)} K_L$

2. The saturated case is realized when

$$K_L \theta_L \gg 1$$

$$\text{i.e. } \theta_L \approx 1 \quad (2.24(a))$$

$$\text{and } \frac{\partial C_L}{\partial C_L} = K_L^* = 0, \quad (2.24(b))$$

These two cases are illustrated in Fig. (7).

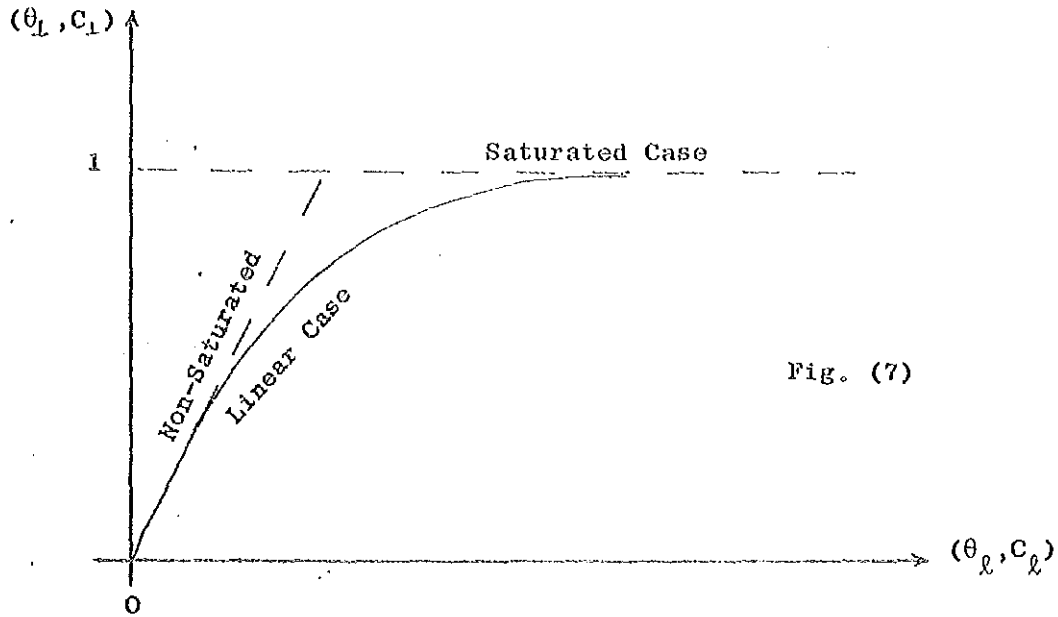


Fig. (7)

The derivation of the differential form of the distribution law given by Eqns. (2.23(b)) and (2.24(b)) will be discussed in chapter-3 section (3.1).

Within the saturated trap regions approach ( $K = 0$ ), Eqn. (2.16) reduces to:

$$D_{\text{eff}} \approx D, \quad (2.25)$$

Thus, it is impossible to describe the experimental results,  $D_e \ll D$ , by such an approach [13]. Moreover, one can conclude that, Sakamoto has not used a "proper" approximation to reduce his complicated equation (2.14) to equation (2.7).

2.4: THE INSUFFICIENCY OF THE COTTRELL MODEL  
FOR THE INTERPRETATION OF THE EXPERIMENTAL  
DATA ON THE IMPURITY DIFFUSION IN DEFORMED  
METALS AND ALLOYS

Most of the authors: Sakamoto, Oriani, Mc Nabb and Foster, Leblond and Dubois... etc, have used the model of the near-dislocation segregation regions with high local diffusivity ( $D_d \gg D$ ) of impurity atoms. This has been explained in-terms of an enhanced jump rates due to lower barriers at trap sites compared with those of normal lattice sites [13,73]. This behaviour corresponds to the cottrell cloud model of impurity segregations in the near-dislocation regions possessing distorted matrix like structure, [72]. The distribution law that represents this model will be considered in chapter-3, Fig. (9).

For the case,  $D_d \gg D$  and  $K_d N_d \gg 1$ , Eqn. (2.16) gives:

$$D_{\text{eff}} \approx D_d \gg D, \quad (2.26)$$

This is an enhancement impurity diffusion which is in contradiction with the experimental data ( $D_e \ll D$ ).

In the cottrell cloud model [72] the maximum value of  $\alpha_d$  has to be less than 10, in order to have the binding energy for the impurity atoms, close to the experimental values of  $\Delta H_d$  (table-III). Thus the experimental values of  $\alpha_d$  and  $\Delta H_d$  for C in Fe (table-III), could be explained within the

the cottrell cloud model, whereas the experimental data on  $\alpha_1$  and  $\Delta H_1$  for C in Fe-3.5%Si, H<sub>2</sub> in Fe-0.16%C and D<sub>2</sub> in Ni cannot be described by this model.

In table-III, one can observe that for all the systems, D<sub>1</sub> has a low value. This follows from the fact that D<sub>e</sub> << D. Such low value of D<sub>1</sub>, however, could not be explained within the frame work of the cottrell model. The analysis of this discrepancy can be seen below.

From Eqn. (2.16) it follows that the reduction of D<sub>eff</sub> to the form of Eqn. (2.7) (corresponding to the experimental data) is possible if:

$$D_1 \ll D \text{ and } K_1 N_1 \geq 1$$

$$\text{ie. } D_{\text{eff}} \approx \frac{D}{1 + N_1 K_1}, \quad (2.27)$$

In other words, this analysis proves that the near-dislocation segregation regions in the systems in question (table-III) possess negligible impurity diffusion, contrary to the cottrell model. One can, therefore, conclude that the cottrell cloud model (for saturated and non-saturated cases) is not sufficient for describing the experimental results on  $\alpha_1$ ,  $\Delta H_1$  and D<sub>1</sub>.

To resolve such discrepancy, it is expedient to formulate some different model of the near-dislocation

phase segregation regions with compound-like structure such as intermetallic compounds (carbides... etc.). The relevance of such a model will be discussed in the next two chapters.

The above conclusions have been done based on the proper reduction of the Sakamoto equation (2.14) to Eqn. (2.7). In the next chapter a similar equation as Eqn. (2.7) will be obtained by two independent methods (approaches). One of these approaches contains the original consideration of the impurity diffusion accompanying phase transition in the near-dislocation regions.

**Table IV: The Techniques for the Observation of Dislocations [92]**

1. Surface methods: in which the point of emergence of dislocation at the surface of a crystal is revealed.
2. Decoration Methods: for examining dislocations in bulk crystals transparent to light.
3. Transmission Electron Microscopy: in which the dislocations are studied in specimens 1000-10,000<sup>0</sup>Å thick.
4. X-ray Diffraction: which relies on local differences at dislocations in the scattering of X-rays.
5. Field Ion Microscopy: which reveals the position of the individual atoms.

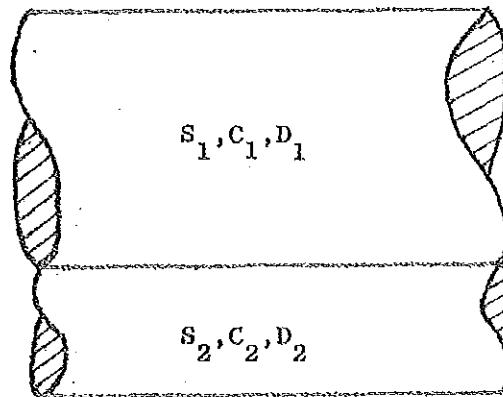
## CHAPTER III

### THE DEVELOPMENT OF THE MODEL

#### 3.1:- THE EFFECTIVE DIFFUSION COEFFICIENT IN CRYSTALS WITH DISLOCATIONS DECORATED BY IMPURITY SEGREGATIONS

In view of the preceding discussions on experimental data, some phenomenological considerations of the corresponding diffusion equation is expedient to obtain the expression for the effective diffusion coefficient of an impurity in crystals with dislocations decorated with impurity segregation phases.

According [17], a one-dimensional diffusion of an impurity, along two neighbouring parallel regions of the same length having different cross-sectional areas ( $S_1, S_2$ ), different impurity concentrations ( $C_1, C_2$ ) and diffusion coefficients ( $D_1, D_2$ ), has been considered as shown in Fig. (8).



(Fig. (8))

$$S_1 \gg S_2, \quad \frac{S_2}{S_1 + S_2} \approx \frac{S_2}{S_1} = N_2$$

In the case of local equilibrium with respect to the process of the impurity distribution between the two regions which is adequate to impenetrable partition, the diffusion equation can be represented as in [17].

$$\text{ie. } D_1 \frac{\partial^2 C_1}{\partial X^2} + D_2 N_2 \frac{\partial^2 C_2}{\partial X^2} = \frac{\partial C_1}{\partial t} + N_2 \frac{\partial C_2}{\partial t} \quad (3.1)$$

$$D_1 \frac{\partial^2 C_1}{\partial X^2} + D_2 N_2 \left( \frac{\partial}{\partial X} \frac{\partial C_2}{\partial C_1} \frac{\partial C_1}{\partial X} \right) = \frac{\partial C_1}{\partial t} + N_2 \frac{\partial C_2}{\partial C_1} \frac{\partial C_1}{\partial t}$$

$$\text{If } \frac{\partial C_2}{\partial C_1} = K = \text{constant}, \quad (3.2)$$

$$\text{then, } \left[ \frac{D_1 + D_2 N_2 K}{1 + N_2 K} \right] \frac{\partial^2 C_1}{\partial X^2} = \frac{\partial C_1}{\partial t} \quad (3.3)$$

Eqn. (3.2) gives the differential form of the distribution law, as required. The term in the bracket of Eqn. (3.3), is the effective diffusion coefficient ( $D_{\text{eff}}$ ). The region occupied with dislocations decorated with segregation phases is so small compared to the lattice undisturbed by dislocations ie.  $N_2 \ll 1$ . Subsequently, the effective diffusion coefficient of an impurity in a crystal with dislocations decorated with segregation phases can be approximated as:-

$$D_{\text{eff}} = \frac{D + D_1 N_1 K_1}{1 + N_1 K_1}$$

$$D_{\text{eff}} = \frac{D}{1 + N_1 K_1} \left[ 1 + \frac{D_1 N_1 K_1}{D} \right], \quad (3.4)$$

which corresponds to Eqn. (2.16) in Chapter-2.

### 3.2:- THE CONSIDERATION OF SOME SUITABLE DISTRIBUTION LAW OF IMPURITIES BETWEEN THE NEAR-DISLOCATION REGIONS AND THE MATRIX

In Chapter-2, it has been shown that the Cottrell cloud model is not sufficient for the interpretation of the experimental data on the impurity diffusion in deformed metals. It is essential, therefore, to consider a model of segregation phases in the near-dislocation regions formed as a result of the "condensation" of the Cottrell clouds.

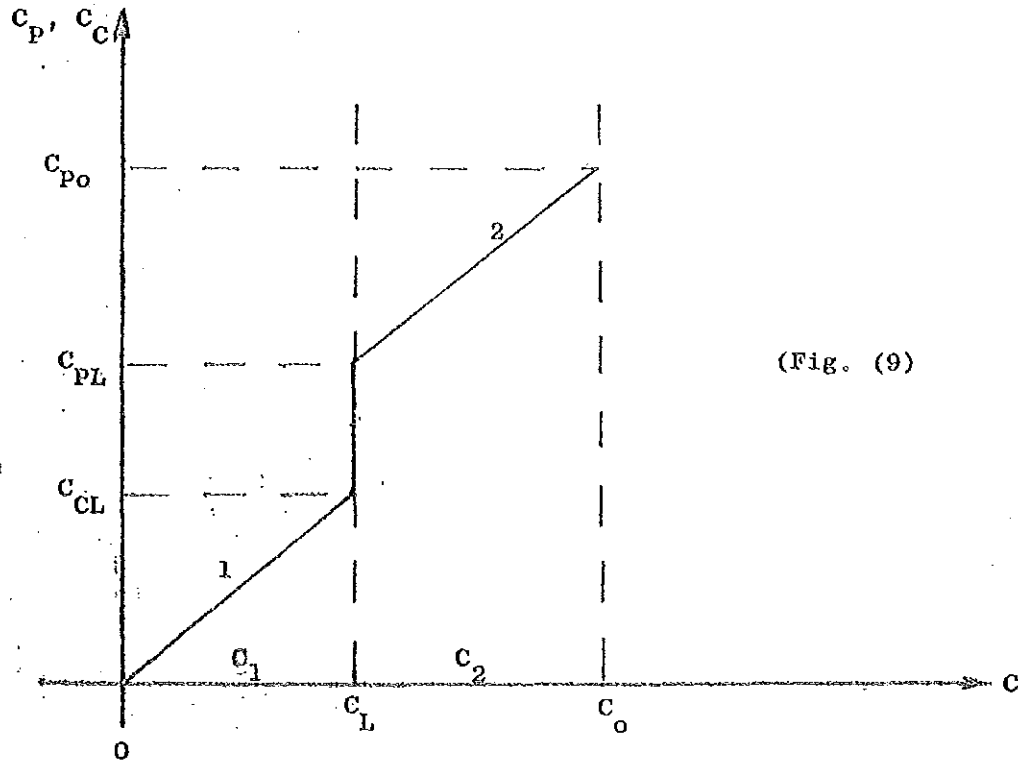
From Eqn. (3.2) it follows that, the relevant distribution law should have a "linear" concentration dependence,

$$\text{ie. } C_2 = \lambda + KC_1, \quad (3.5)$$

where;  $\lambda$  and  $K$  are constants.

Using Eqn. (3.5) the "linear" dependence behaviour of the impurity concentration in the segregation phase

and the Cottrell Cloud on the matrix solution at constant temperature is illustrated in Fig. (9).



(Fig. (9))

C is the impurity concentration in the matrix, such that:-

$$C = C_1, 0 \leq C \leq C_L$$

$$C = C_2, C_L \leq C \leq C_0$$

$C_0$  is the equilibrium solubility of impurity in the matrix (at given T) with respect to the corresponding compound.

$C_L$  is the impurity concentration in the matrix solution at the segregation phase-Cottrell Cloud boundary.

$C_2$  is the impurity concentration in the matrix.

### 3.3 THE IMPURITY DIFFUSION ACCOMPANYING SOME PHASE TRANSITION IN THE NEAR- DISLOCATION REGIONS

In light of all the discussions of the experimental data and their interpretations based on the concepts [4,5,13,17,71] in the preceding sections, it is useful to consider detailed analysis of the problem of impurity diffusion accompanying segregation phase nucleation on dislocation. This problem could be solved within the approximation of the distribution law considered in section (3.2).

To formulate a model that describes such a phenomenon, one can consider impurity diffusion from a plate surface at  $X=0$ , into a semi- finite specimen (matrix) containing a regular array of dislocations as shown in Fig.(10). All dislocations are normal to the surface, each represented as a "pipe" of radius  $r_s$ , where the segregation phases or the cottrell clouds are nucleated. These regions have a composition that depends on the impurity concentration in the matrix solution as illustrated in Fig. (9).

It is convenient to divide the specimen into independent diffusion cells. Each cell is a semi- finite cylinder whose axis coincides with a dislocation "pipe" (Fig. (10)). Let the diameter of the cell be  $2R$  which

is equal to the mean separation between neighbouring dislocations such that  $2R \approx \rho_d^{-1/2}$  and  $R \gg r_s$ . Assume a constant impurity concentration ( $C_0$ ) in the matrix solution maintained at the surface  $X=0$  (Fig. (9)). Let at time  $t$  (from the starting of the diffusion annealing) the segregation phase regions along dislocations with radius  $r_s$ , have some mean length of  $L$  (Fig. (10)). The impurity concentration in the matrix solution, (in the neighbourhood of the segregation phase regions) at  $X=L$ , equals some constant value  $C_L < C_0$  (Figs. (9) and (10)). At the same time,  $t$ , for  $X > L$ , the impurity concentration in the matrix solution,  $C$ , is less than  $C_L$ , and in the near-dislocation regions of radius  $r_s$  the Cottrell cloud is formed.

Using the approximation of the local equilibrium with respect to the impurity distribution between the two regions in every cell, and the distribution law with linear concentration dependence [5,17,74], the diffusion problem can be reduced to unidimensional as follows:-

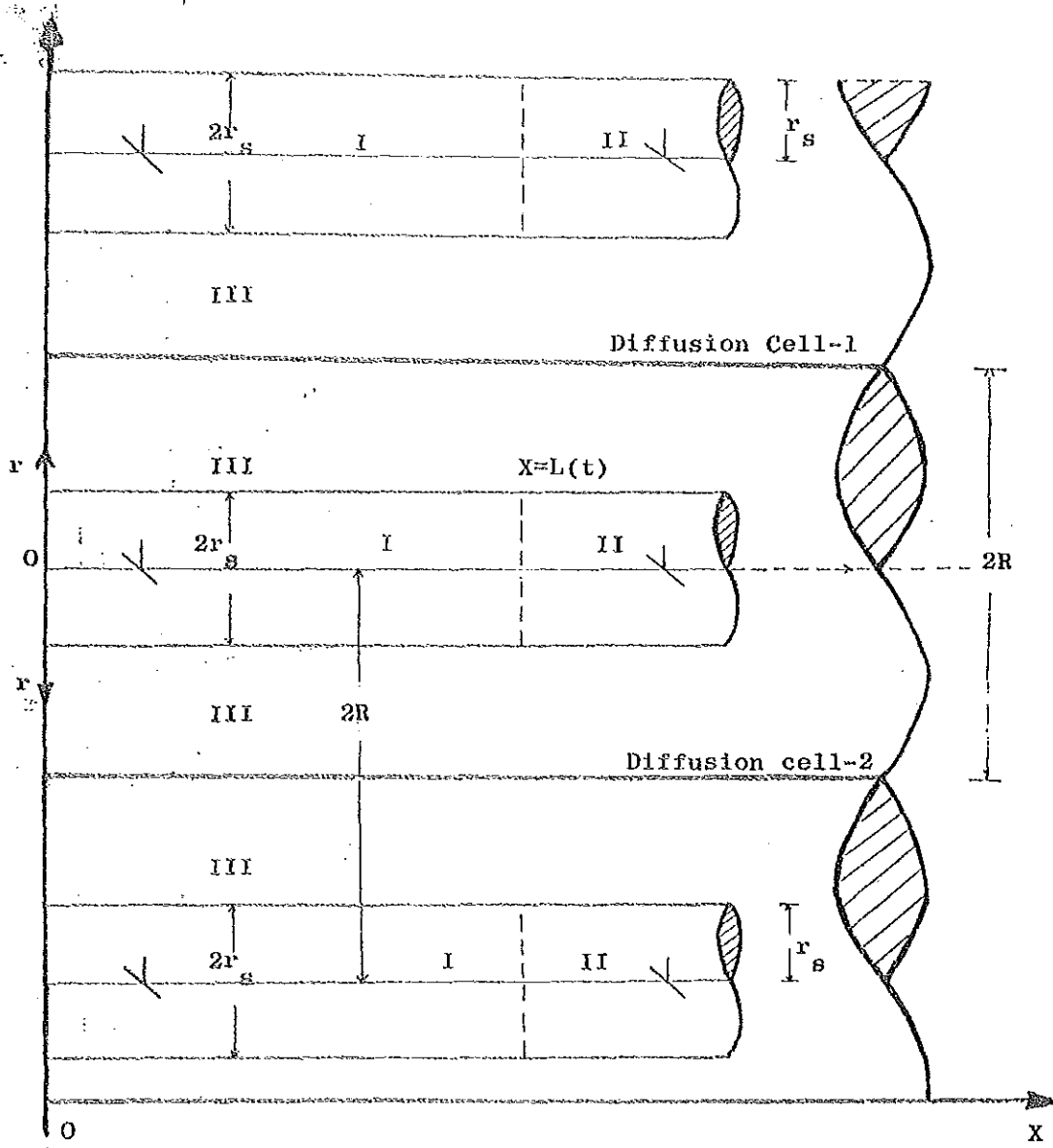
For the region  $0 < X < L$  (Fig. (10)) the distribution law can be taken as Eqn. (3.7).

$$\text{ie, } C_p = C_{PL} + K_2 (C_2 - C_L)$$

$$N_t \{ C_p = C_{PL} + K_2 (C_2 - C_L) \}$$

$$N_p = N_{PL} + \gamma_2 (C_2 - C_L) \quad , \quad (3.8)$$

Fig. 10: Impurity diffusion from a plate surface at  $X=0$ , into a semi-finite specimen containing a regular array of dislocations.



- I: Represents the segregation phase region.
- II: Represents the Cottrell cloud region.
- III: Represents the Matrix Section.

Where:  $N_t \approx (r_s/R)^2$ , (Fig. -10);  $K_2$  is the equilibrium constant of the impurity distribution between segregation phase regions along dislocations and the matrix solution;  $C_{PL}$  is the impurity concentration in the segregation phase regions at  $X=L$ , corresponding to the solubility  $C_L$ , such that  $C_{PL} \gg C_L$  (Fig. 9);  $C_2$  is the impurity concentration in the matrix solution ( $C_L < C_2 < C_0$ ).

In this approximation the diffusion equation for the region  $0 < X < L$ , can be represented as Eqn. (3.1) and (3.2).

$$\text{ie. } (D_P \gamma_2 + D) \frac{\partial^2 C_2}{\partial X^2} = (1 + \gamma_2) \frac{\partial C_2}{\partial t}, \quad (3.9(a))$$

$$C_2(0, t) = C_0, \quad C_2(X, 0) = 0, \quad (3.9(b))$$

Where:  $D$  is the impurity diffusion coefficient in the matrix solution containing no dislocations;  $D_P$  is the impurity diffusion coefficient in the near-dislocation segregation phase regions and

$$\gamma_2 = K_2 N_t$$

For the region  $L < X < \infty$ , the distribution law can be expressed as Eqn. (3.6).

$$\text{ie. } C_0 = K_1 C_1$$

$$N_t \{C_0 = K_1 C_1\}$$

$$N_c = \gamma_1 C_1, \quad (3.10)$$

Where:  $K_1$  is the constant of equilibrium for the process of the impurity distribution between the Cottrell cloud regions along dislocations and the matrix solution and  $C_1$  is the impurity concentration in the matrix solution ( $0 \leq C_1 \leq C_L$ )

The diffusion equation for the region  $L < X < \infty$ , can be written as Eqn. (3.1) and (3.2).

$$\text{ie. } (D_c \gamma_1 + D) \frac{\partial^2 C_1}{\partial X^2} = (1 + \gamma_1) \frac{\partial C_1}{\partial t}, \quad (3.11(a))$$

$$C_1(X, 0) = 0, \quad C_1(\infty, t) = 0, \quad (3.11(b))$$

Where:  $D_c$  is the impurity diffusion coefficient in the Cottrell cloud regions along dislocations and  $\gamma_1 \approx K_1 N_d$ .

As illustrated in [75], the problem of impurity diffusion accompanying segregation phase nucleation on dislocation can be reduced to the problem of linear diffusion equations for regions separated by unknown moving boundaries.

In the neighbourhood of the moving boundary of the segregation phases and the Cottrell Clouds, ie.  $X_2 < (X=L(t)) < X_1$ , one can assume that the concentration function is piece-wise smooth. Hence integrating the sum of Eqn. (3.9(a)) and (3.11(a)) it follows that:-

$$\begin{aligned} (N_{PL} - N_{CL}) \frac{dL}{dt} = & - (D_P \gamma_2 + D) \left. \frac{\partial C_2}{\partial X} \right|_{X=L} , & (3.12)** \\ & + (D_C \gamma_1 + D) \left. \frac{\partial C_1}{\partial X} \right|_{X=L} \end{aligned}$$

At  $X=L$ :  $C_1(L, t) = C_2(L, t) = C_L$

Where:  $N_{PL} = C_L \gamma_2$  and  $N_{CL} = C_L \gamma_1$

To solve the differential equation for a semi-finite specimen, it is legitimate to consider dimensionless variables as:-

$$\xi_1 = \frac{X}{2\sqrt{(D_C \gamma_1 + D)t}} , \quad \xi_2 = \frac{X}{2\sqrt{(D_P \gamma_2 + D)t}} , \quad (3.13)$$

and to make things easier, let:

$$C_1^* = C_1/C_0 , \quad C_2^* = C_2/C_0 \text{ and } C_L^* = C_L/C_0 , \quad (3.14)$$

Thus by using Eqns. (3.13), (3.14) and the known solutions for the diffusion problem of a semi-finite specimen with constant impurity concentration at the surface, one can obtain:

$$C_2^*(\xi_2) = 1 - \frac{(1 - C_L^*) \operatorname{erfc}(\xi_2 \sqrt{1 + \gamma_2})}{\operatorname{erfc}(\xi_{02} \sqrt{1 + \gamma_2})} \quad (3.15)$$

$$C_1^*(\xi_1) = \frac{C_L^* \operatorname{erfc}(\xi_1 \sqrt{1 + \gamma_1})}{\operatorname{erfc}(\xi_{01} \sqrt{1 + \gamma_1})} \quad (3.16)$$

\*\*

The derivation of Eqn. (3.12) is given in Appendix-A.

$$\text{where: } \xi_{01} = \frac{\beta}{2\sqrt{(D_C\gamma_1 + D)}}, \quad \xi_{02} = \frac{\beta}{2\sqrt{(D_P\gamma_2 + D)}}, \quad (3.17)$$

$$\text{and } L(t) = \beta\sqrt{t}, \quad (3.18)**$$

Equations (3.15) and (3.16) are the desired solutions of the diffusion problem, since they satisfy, all the initial and boundary conditions given by Eqns. (3.9(b)) and (3.11(b)).

From Eqn. (3.17) it follows that:

$$\xi_{02} = \left( \frac{D_C\gamma_1 + D}{D_P\gamma_2 + D} \right)^{\frac{1}{2}} \xi_{01}, \quad (3.19)$$

ie. there is only one parameter  $\xi_{01}$  or  $\beta$  to be determined. Using Eqns. (3.12) — (3.19) one can obtain the transcendental equation by which  $\xi_{01}$ , ( $\beta$ ), are determined (by graphical method).

$$\text{ie. } \frac{\sqrt{D_2/D_1(1+\gamma_2)} (1-C_L^*) \exp \left[ -\frac{D_1}{D_2}(1+\gamma_2) \xi_{01}^2 \right]}{\text{erf} \left[ \sqrt{D_1/D_2(1+\gamma_2)} \xi_{01} \right]} \quad (3.20)$$

$$= \frac{\sqrt{(1+\gamma_1)} C_L^* \exp \left[ -(1+\gamma_1) \xi_{01}^2 \right]}{\text{erfc} \left( \xi_{01} \sqrt{(1+\gamma_1)} \right)} = \sqrt{\pi} a_L \xi_{01}$$

$$\text{where: } D_1 = (D + D_C\gamma_1), \quad D_2 = (D + D_P\gamma_2)$$

$$\text{and } a_L = (N_{PL} - N_{CL}).$$

\*\* The derivation of Eqn. (3.18) is given in appendix-B.

But the objective of this paper is to obtain an expression for the effective diffusion coefficient in the usual treatment of the experimental data on penetration profiles. Thus if:  $\gamma_2 \gg 1$ ,  $C_L^* \ll 1$  and  $\xi_{02} \sqrt{\gamma_2} \geq 2$ , then Eqn. (3.15) reduces itself to the generally accepted expression that describes the concentration profile in the region  $0 < X < L$ .

$$\text{ie. } C_2(X,t) = C_0 \{1 - \text{erf} [X/2 \sqrt{D_{\text{eff}} t}]\}, \quad (3.21)$$

$$\text{where: } D_{\text{eff}} = \frac{D + D_P \gamma_2}{1 + \gamma_2}, \quad (3.22)$$

Which is the same as Eqn. (2.16).

This coincidence shows that the application of Eqn. (3.22) is valid for the following two cases.

1. The case where the near-dislocation regions are decorated by some segregation phases before the impurity diffusion.
2. The case where the impurity diffusion is accompanied by the nucleation of the segregation phases in the near-dislocation regions, provided the phase transition is not dominant.

## CHAPTER IV

### 4.1 THERMODYNAMIC AND CRYSTALLOGRAPHIC ANALYSIS OF THE APPLICABILITY OF THE MODEL

As it has been shown in the preceding chapters, the treatment of the experimental data on the impurity diffusion and solubility in cold-worked metals and alloys (table-III), based on the dislocation trap model, allows one to determine some characteristics of the near-dislocation trap regions. The Cottrell segregation model, however, cannot give a satisfactory explanation of these characteristics, namely:

1. High values of  $\alpha_1$ ,  $\Delta H_1$  and  $C_1$  (table-III) corresponding to the distribution law with linear concentration dependence.
2. Anomalously low values of the impurity diffusion coefficient ( $D_1$ ) in the near-dislocation trap regions ( $D_1 \ll D$ ).

There are some experimental data showing the possibility of the existence of the segregation phase regions along dislocations in the systems in question.

As noted by J. Friedel [83], a number of measurements indicate that at low temperatures, dislocations (in Fe-crystals) can attract considerable amount of impurity atoms (C,N), possibly more than 40 atoms per dislocation line per atomic plane ( $n_{11}$ ).

According to Christian [84], at low temperatures in metals (Fe), a large number of interstitial impurity atoms gather per atomic plane crossing a dislocation line ( $n_{il}$ ). For instance the experimental data [85] on the cold-worked specimens of:

- i) Nb --- 0.9 wt% O, at 413<sup>o</sup>K, gives  $n_{il}$  about 30 (for oxygen atoms).
- ii) Nb --- 0.9 wt% N at 473<sup>o</sup>K,  $n_{il}$  is about 70 (for nitrogen atoms).

These values of  $n_{il}$  [83-85] are greater by (1-2) orders than the theoretical and experimental values of  $n_{il}$  corresponding to the Cottrell model [72]. These values are rather suitable for the segregation phase model [17].

In this work, the number of captured impurity atoms per dislocation line per atomic plane can be estimated as:

$$n_{il} \approx \alpha C_d, \quad (4.1)$$

Thus the range for the values of  $n_{il}$ , from the data on  $\alpha_d$  and  $C_d$  in table-III, will be:

1.  $10 \sim 1$ , (C in  $\alpha$ -Fe)
2.  $10 \sim 1$ , (C in Fe-3.5 wt% Si)
3.  $20 \sim 2$ , ( $H_2$  in Fe-0.16 wt% C)
4.  $1 \sim 0.1$ , ( $D_2$  in Ni).

One can describe all the characteristics ( $\alpha_d$ ,  $\Delta H_d$ ,  $C_d$ ,  $D_d$  and  $n_{il}$ ) satisfactorily by the developed model based on the analysis of the results in table-III, using thermodynamic and crystallographic methods.

Firstly, the results on diffusion and solubility of

C in  $\alpha$ -Fe can be described within the model of impurity diffusion accompanying the formation of carbide-like structure in the near-dislocation regions. This model has been considered in chapter-3 section (3.3). The solubility of the  $Fe_3C$  compound in Fe crystal can be described by the formula [86].

$$C_{[i]} = \exp \left( \frac{\Delta S_d}{R} \right) \exp \left( - \frac{\Delta H_d}{RT} \right), \quad (4.2)$$

Where:-  $C_{[i]}$  is the atomic fraction of the impurity atoms in the matrix solution saturated with respect to the compound phase at a given temperature  $T$ ,  $\Delta H_d$  and  $\Delta S_d$  are the enthalpy and entropy of dissolution of the compound in the matrix respectively.

Within the frame work of the theory of thermodynamics of dilute solutions [86] it follows that:

$$\Delta H_d = \Delta \bar{H}_{[i]} - \Delta H_f^0, \quad (4.3)$$

$$\Delta S_d = \Delta \bar{S}_{[i]} - \Delta S_f^0, \quad (4.4)$$

Where:-  $\Delta \bar{H}_{[i]}$  and  $\Delta \bar{S}_{[i]}$  are relative partial molar enthalpy and entropy of impurity atoms in the matrix solution, respectively,  $\Delta H_f^0$  and  $\Delta S_f^0$  are the standard enthalpy and entropy of the formation of one mole of the compound from the chemical elements.

Some results of literature data on the thermodynamic characteristics of compounds are represented in table- V. From tables-III, and V, it follows that for the case of C in  $\alpha$ -Fe the experimental value of  $\Delta H$  is larger than  $\Delta H_d$

by  $18 \pm 6$  KJ/mol. This difference could be accounted for the influence of the dislocation stress field, on the dissolution process of the compound. According to the model, the compound like-structure ( $\text{Fe}_3\text{C}$ ) is localized in the near-dislocation regions with cross-sectional diameter of about  $\sqrt{ab} \approx 10\text{\AA}$ . For edge dislocations, the local pressure (due to the normal stress components) in these regions could be estimated as [72].

$$P_d \approx \frac{1+\nu^*}{1-\nu^*} \frac{\mu b}{3\pi r} \quad (4.5)$$

$$\text{and } r \approx \frac{\sqrt{ab}}{2} \quad (4.6)$$

Where:  $\mu$  is modulus constant  $\approx 8.6 \times 10^{10} \text{ N/m}^2$  (for  $\alpha\text{-Fe}$ );  $\nu^*$  is Poisson ratio  $\approx 0.291$ .

By substituting the given values, one can have:  $P_d \approx 1 \times 10^{10} \text{ N/m}^2$ . Then the contribution to  $\Delta H_d$  could be estimated as [72].

$$\Delta H \approx \Delta H_d + P_d \Delta V \quad (4.7)$$

$$\text{and } \Delta H \approx 3V_{\text{Fe}} - V_{\text{Fe}_3\text{C}} \quad (4.8)$$

$$\text{Where: } V_{\text{Fe}_3\text{C}} \approx 23 \text{ cm}^3/\text{mol} \quad [87]$$

$$V_{\text{Fe}} \approx 8 \text{ cm}^3/\text{mol} \quad [87]$$

Thus,  $P_d \Delta V \approx 10 \text{ KJ/mol}$ , which is the desired result.

In this approximation, the surface tension ( $\sigma$ ) effect has been neglected for the following crystallographic assumptions.

According to [17,88,89] one of the main factors of nucleation of the segregation phase regions near-dislocations is the negligible low value of the surface tension ( $\sigma$ ), at the interface of the segregation phase and the matrix.

The low value of  $\sigma$ , in the case of compounds:  $\text{Fe}_3\text{C}$  ( $\text{Ni Al}_3$ ),  $\text{Fe}_2\text{C}$  and  $\text{Fe}_{20}\text{C}_9(\text{PdAl}_3)$  could arise from the amorphization of the near-dislocation segregation phases resulting from the existence of empty trigonal bipyramids of the Bernal type in the structure of these compounds. Fig. 11. According to Bernal's model [90] which has been interpreted by Pinskner [91], the amorphous packing with sufficiently high density of filling is formed by trigonal bipyramids sharing the faces.

Obviously, in these structures (Fig. 11) some amorphous zones having no long-range order may occur, located near the edge dislocation regions. It could be suggested that the higher the amorphization degree of the near-dislocation segregation phases in matrix (metals) is, the lower the surface tension at the interface of the segregation phase and the matrix will be.

Such structures could possess low values of the impurity diffusivity in comparison with the matrix (Fe) structure ie.  $D_1 \ll D$ . Thus all the near-dislocation characteristics ( $\alpha_1$ ,  $\Delta H_1$  and  $D_1$ ) of C in  $\alpha$ -Fe can be interpreted within this model. The linear character of the impurity distribution law, for such a case, can be explained as follows: The

atomic fraction of the carbon atoms in the matrix solution in equilibrium with the segregation phases of Fe<sub>3</sub>C-like structure in the near-dislocation regions, can be represented as:

$$C \approx \exp (-\Delta H/RT) , \quad (4.9)$$

Where:  $\Delta H \approx \Delta H_d + P_d \Delta V$

when most of the impurity is located in the near-dislocation segregation regions (ie.  $K_d N_d \gg 1$ ), the impurity distribution law can be described as:-

$$\frac{C_d N_d}{C} = \frac{C_\epsilon - C}{C} \approx \frac{C_\epsilon}{C} , \quad (4.10)$$

$$\frac{C_d}{C} \approx A \exp (\Delta H/RT) , \quad (4.11)$$

where:  $A = C_\epsilon / N_d$

Hence, it follows that the impurity distribution may correspond to Eqn. (3.2) which was employed to obtain Eqn. (3.4) and (3.22).

Secondly, for the systems: C in Fe-3.5 wt% Si, H<sub>2</sub> in Fe-0.16 wt% C and O<sub>2</sub> in Ni (table-III), however, different situations are realized. That is the values of C<sub>d</sub> in table-III, indicate that the local impurity concentration of the systems do not correspond to the carbide-like structure (C in Fe) or hydride-like structures (H<sub>2</sub> in Fe, O<sub>2</sub> in Ni). But at the same time large values of  $\alpha_1$  and

low values of  $D_i$  show the possibility of the formation of the compound-like structure in the near-dislocation regions.

For the system  $D_2$  in Ni it could be assumed that the impurity diffusion was accompanied by the phase transition such as: Ni-FCC to Ni-HCP (Hexagonal Closed Packed structure) or to Ni-FCT (Face-Centered Tetragonal structure) in the near-dislocation regions. This follows from the experimental data [87] in which the presence of hydrogen atoms with concentration,  $10^{-2} - 10^{-3}$ , the stable structure of Ni-lattice is HCP or FCT instead of FCC. This could be described by using Eqn. (3.22).

For the system C in Fe-3.5 wt%Si one can assume that in the near-dislocation regions, the segregation phases of Fe Si-like structure were existing before the impurity (C) diffusion. This assumption is consistent with the large negative value of the heat of formation,  $\Delta H_f^0$ , of the Fe Si compound (table V). During the impurity diffusion, the composition of the near-dislocation segregation regions could change particularly due to the strong interaction of carbon atoms with silicon. (see  $\Delta H_f^0$  of Si C table V).

For the case of  $H_2$  in Fe-0.16 wt% C (steel) it could be assumed that, in the near-dislocation regions, segregation phases of the  $Fe_3C$  compound-like structure were existing before the impurity diffusion. The last two systems, therefore, can be described by using Eqn. (3.4).

Summing up, the analysis made in this chapter shows the applicability of the developed model, for the interpretation of the known experimental data on impurity diffusivity and solubility in deformed metals and alloys.

Table V: Thermodynamic characteristics of some intermetallic compounds and substances

Substance	$H_d,$ KJ/mol	$\Delta S_d/R$	$\Delta H_f^0,$ KJ/mol	$\Delta S_f^0/R$	$\Delta \bar{H}_{[i]},$ KJ/mol	$\frac{\Delta \bar{S}}{R} [i]$
C, Fe <sub>3</sub> C in α-Fe	39±4 [72]	-2 [72]	23±4 [87]	1.4 [87]	62±6	-0.6
Fe Si			-80±15 [87]			
SiC			-63±13 [87]	-2.1 [87]		

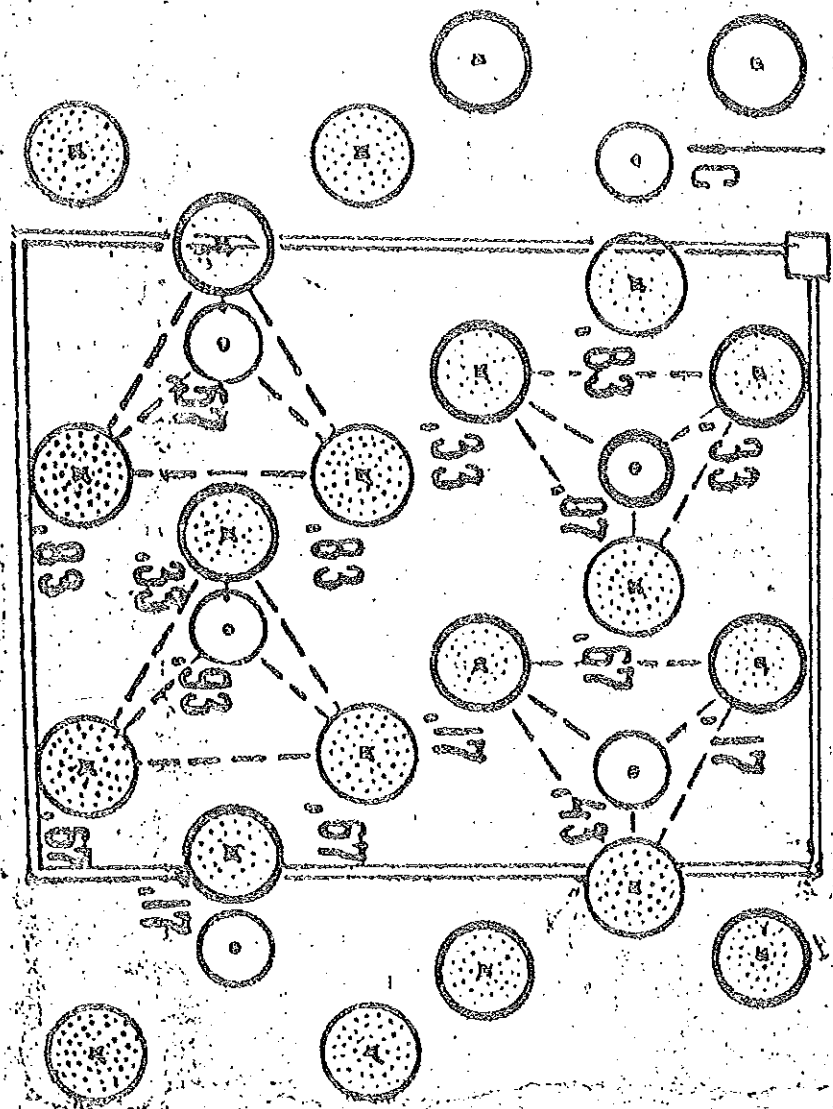


Fig. 11: The structure of the  $Fe_3C$  interstitial compound contains trigonal bipyramides zones of possible amorphization near-dislocations.

[1].

CONCLUSIONS

1. Development of the theory of dislocation influence on impurity diffusivity and solubility has been done. The problem of impurity diffusion accompanied with segregation phase nucleation on dislocations has been solved. The diffusion-with-trapping-effect and diffusion-by-dislocation effect have been considered.
2. It has been shown that in the known theoretical models of impurity diffusion in deformed metals, the diffusion-by-dislocation-effect has been neglected. This assumption was based on a wrong approximation of the "trap-saturation-model" and even without any physical reason.
3. On the basis of the analysis of the known experimental data on impurity solubility, and diffusivity in deformed metals using the developed model, the characteristics of the near-dislocation segregation regions have been obtained for four systems; namely C in  $\alpha$ -Fe, C in Fe-3.5% Si, H<sub>2</sub> in Fe-0.16%C and D<sub>2</sub> in Ni.

In particular, it has been shown that the impurity segregation regions near-dislocations possess negligible diffusion conductivity and high capture ability for interstitial impurities at low temperatures.

4. On the basis of thermodynamic and crystallographic analysis, the acceptability of the model of the segregation phases in the near-dislocation regions (with compound-like structure) for systems considered has been shown.

RECOMMENDATIONS

1. By using the model of the impurity diffusion accompanying some phase transition in the near-dislocation regions, all known literature data on impurity diffusivity and solubility in deformed metals and alloys (such as N and O) could be interpreted.

2. The compound-like structure of the near-dislocation segregation regions for systems considered could be investigated using an electron-microscopy technique and others.

APPENDIX

A. THE DERIVATION OF EQN. (3.12)

In the neighbourhood of the moving boundary of the segregation phases and the cottrell cloud i.e.  $X_2 < (X=L(t)) < X_1$ , one can assume that the concentration function is piece-wise smooth. Hence integrating the sum of Eqns. (3.9(a)) and (3.11(a)), gives:

$$\int_{X_2}^{X_1} \left\{ (1+\gamma_2) \frac{\partial C_2}{\partial t} + (1+\gamma_1) \frac{\partial C_1}{\partial t} \right\} dX$$

$$= \int_{X_2}^{X_1} \left\{ (D_P \gamma_2 + D) \frac{\partial^2 C_2}{\partial X^2} + (D_C \gamma_1 + D) \frac{\partial^2 C_1}{\partial X^2} \right\} dX,$$

$$\frac{d}{dt} \int_{X_2}^{X_1} \left\{ (1+\gamma_2) C_2 + (1+\gamma_1) C_1 \right\} dX$$

$$= \int_{X_2}^{X_1} \left\{ (D_P \gamma_2 + D) \frac{\partial^2 C_2}{\partial X^2} + (D_C \gamma_1 + D) \frac{\partial^2 C_1}{\partial X^2} \right\} dX,$$

$$(1+\gamma_2) \frac{d}{dt} \left\{ \int_{X_2}^L C_2 dX \right\} + (1+\gamma_1) \frac{d}{dt} \left\{ \int_L^{X_1} C_1 dX \right\}$$

$$= \int_{X_2}^L (D_P \gamma_2 + D) \frac{\partial^2 C_2}{\partial X^2} dX + \int_L^{X_1} (D_C \gamma_1 + D) \frac{\partial^2 C_1}{\partial X^2} dX,$$

$$(1+\gamma_2) \frac{d}{dt} \{ C_2 [L - X_2] \} + (1+\gamma_1) \frac{d}{dt} \{ C_1 [X_1 - L] \}$$

$$= (D_P \gamma_2 + D) \frac{\partial C_2}{\partial X} \Big|_{X=X_2}^{X=L} + (D_C \gamma_1 + D) \frac{\partial C_1}{\partial X} \Big|_{X=L}^{X=X_1}$$

As  $\Delta X = (L - X_2) = (X_1 - L)$  approaches zero,  $(L - X_2)$  and  $(X_1 - L)$  will approach zero. Thus the above expression will reduce to:

$$(1 + \gamma_2) \{ C_2 \frac{d}{dt} [L - X_2] \} + (1 + \gamma_1) \{ C_1 \frac{d}{dt} [X_1 - L] \}$$

$$= (D_P \gamma_2 + D) \frac{\partial C_2}{\partial X} \Big|_{X=L} - (D_P \gamma_2 + D) \frac{\partial C_2}{\partial X} \Big|_{X=X_2}$$

$$+ (D_C \gamma_1 + D) \frac{\partial C_1}{\partial X} \Big|_{X=X_1} - (D_C \gamma_1 + D) \frac{\partial C_1}{\partial X} \Big|_{X=L}$$

From the continuity equation the flux is continuous

$$\text{i.e. } (D_P \gamma_2 + D) \frac{\partial C_2}{\partial X} \Big|_{X=L} = (D_C \gamma_1 + D) \frac{\partial C_1}{\partial X} \Big|_{X=L},$$

and  $X_1$  and  $X_2$  are time independent.

$$\text{Thus: } (1 + \gamma_2) C_2 \frac{dL}{dt} - (1 + \gamma_1) C_1 \frac{dL}{dt}$$

$$= - (D_P \gamma_2 + D) \frac{\partial C_2}{\partial X} \Big|_{X=X_2} + (D_C \gamma_1 + D) \frac{\partial C_1}{\partial X} \Big|_{X=X_1}$$

$$\{ (1 + \gamma_2) C_2 - (1 + \gamma_1) C_1 \} \frac{dL}{dt} = - (D_P \gamma_2 + D) \frac{\partial C_2}{\partial X} \Big|_{X=X_2}$$

$$+ (D_C \gamma_1 + D) \frac{\partial C_1}{\partial X} \Big|_{X=X_1}$$

$$\text{At } X = L: C_1(L, t) = C_2(L, t) = C_L$$

$$(C_{LY2} - C_{LY1}) \frac{dL}{dt} = - (D_P \gamma_2 + D) \frac{\partial C_2}{\partial X} \Big|_{X=L} + (D_C \gamma_1 + D) \frac{\partial C_1}{\partial X} \Big|_{X=L}$$

$$\text{ie. } (N_{PL} - N_{CL}) \frac{dL}{dt} = - (D_P \gamma_2 + D) \frac{\partial C_2}{\partial X} \Big|_{X=L} + (D_C \gamma_1 + D) \frac{\partial C_1}{\partial X} \Big|_{X=L}$$

as required.

B. THE DERIVATION OF EQN (3.18):

As illustrated in [76]:

$$C = C_0 \operatorname{erfc} [X/2(D^* t)^{\frac{1}{2}}]$$

Where:  $D^* = (D_P \gamma_2 + D), (D_C \gamma_1 + D)$

then  $\frac{C}{C_0} = \operatorname{erfc} [X/2(D^* t)^{\frac{1}{2}}],$

$C/C_0$  being constant

ie.  $\operatorname{erfc} [X/2(D^* t)^{\frac{1}{2}}] = \text{const.}$

or  $X = \text{const } (D^* t)^{\frac{1}{2}}$

and  $X \Big|_{C_L/C_0 = \text{const.}} = L = \text{const } (D^* t)^{\frac{1}{2}}$

ie.  $L(t) = (\text{const } \sqrt{D^*}) \sqrt{t}$ , as required

where  $\beta = (\text{const } \sqrt{D^*})$

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