

Molecular diffusion at surfaces

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Introduction:

Diffusion is the net action of matter (particles or molecules), heat, momentum, or light whose end is to minimize a concentration gradient. The process of diffusion, therefore, minimizes thermodynamic Gibbs free energy (though, it is not a chemical reaction), and is thus a spontaneous process (more familiarly known as a "passive" form of transport, rather than "active").

The different forms of diffusion can be modeled quantitatively using the diffusion equation, which goes by different names depending on the physical situation. In all cases of diffusion, the net flux of the transported quantity (atoms, energy, or electrons) is equal to a physical property (diffusivity, thermal conductivity, electrical conductivity) multiplied by a gradient (a concentration, thermal, electric field gradient).

1. Surface Diffusion

Surface diffusion (SD) is a really common phenomenon playing a highly important part in the field of science and technology. The effect of SD is to move surface atoms, molecules and clusters and allow them to assemble into some desirable configurations or, vice versa, to destroy the configurations that have been purposely created. There exists many processes where surface diffusion has a significant role to play as the growth of crystals and thin films; catalysis; sintering and powder metallurgy; capillary phenomena; corrosion; nanotechnologies of all kinds; strengthening of materials; soldering; a multitude of processes that occur on various biological interfaces, etc.

Two types of surface diffusion can play important roles in coverage and deposition layers; bulk diffusion, which is the global macro-motion of the material within the deposited layer, and surface diffusion, which relates to the motion of metal boundaries.

Surface diffusion is a many body or collective phenomenon. Even in the case when we are able to trace the activities of a single atom, one should realize the effect of its motion or activity is solely because of its continuous interaction with the substrate atoms. To understand the phenomenon explained above let us look into the discussion following in the next page.

In the figure given below the atom receives fluctuatively some excessive energy from the substrate. This enables it to jump from one residence site to another. Second, the jump ends as soon as the excessive energy is given back from the diffusing particle to the substrate (the heat bath)

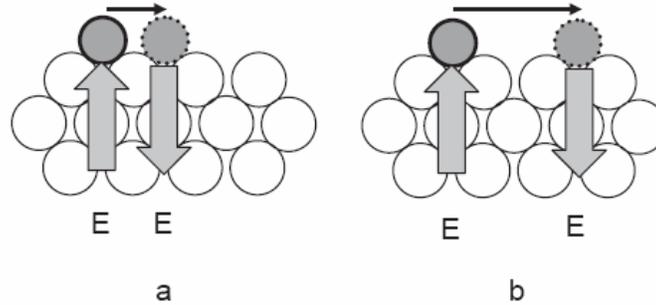


Fig: a) Elementary and b) long jumps of the adsorbed atom on a substrate. E is the corresponding excess energy which the adatom received and given back to the substrate.

1.1 Factors responsible for surface diffusion.

One can attribute the surface diffusion phenomenon to the various lateral interactions developed on the surface. The Van der Waals, direct exchange, indirect exchange and dipole-dipole and higher multipole interactions which are responsible for molecules diffusion at surfaces. These interactions vary in both in their intensity as well as nature. The energies associated in the interactions mentioned above are a function of distance between the ad atoms and substrate.

Van der Waals interaction is attractive and its energy decreases with distance as r^{-6} . The energy of electronic indirect interaction oscillates with distance as the wave functions of interacting adatoms overlap in phase or antiphase. Another kind of the indirect interaction is connected with elastic strains induced in the substrate by the adsorbed layer. The strains arise due to lattice misfit between the substrate and the adlayer. The dipole-dipole interaction, which arises because the adsorption bond may have a considerable dipole moment, decays with distance rather slowly ($\propto r^{-3}$) and plays an important role in many surface phenomenon.

One can conclude with the available information in regard to the various interactions responsible for surface diffusion that:

- (i) SD is basically a many-body process.
- (ii) The kinetics of SD cannot be understood without proper account for interactions between the diffusing particles.
- (iii) SD should be investigated in connection with surface phase transitions.

Kinetics of Surface Diffusion

The diffusion coefficient D is defined as the proportionality constant relating the diffusion flux J to the concentration gradient.

$$J = -D \frac{\partial n}{\partial x}, \text{ where we have assumed concentration } n \text{ depends only on } x.$$

For diffusion of non-interacting species D is just the product of the mean-square jump distance λ^2 and $\Gamma(0)$, the jump frequency of adatoms along the x-direction,

$$D = \Gamma(0)\lambda^2$$

Substituting known expressions for $\Gamma(0)$ and λ^2 , we get the following expression for the diffusion coefficient,

$$D = D_0 \exp(-E_a / kT)$$

With the pre-exponential factor given by

$$D_0 = \nu \exp(\Delta S^\ddagger / k)\lambda^2$$

With the aid of Fick's second law (continuity equation) the diffusion coefficient can be evaluated from the experimental data measured in a concentration gradient:

$$\frac{\partial n}{\partial t} = -\frac{\partial J}{\partial x} = \frac{\partial}{\partial x} \left(D \frac{\partial n}{\partial x} \right)$$

If D depends on x neither explicitly nor via concentration, the latter equation is reduced to

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2}$$

Effect of lateral interactions on SD parameters; thermodynamic factor

In the presence of lateral interactions an additional driving force of diffusion acts together with the concentration gradient. Due to deformations of the potential relief, the frequencies of adatom jumps in opposite directions become unequal. In this case the diffusion flux must be written in a more general form

$$J = -L \frac{\partial \mu}{\partial x},$$

where L is a phenomenological transport coefficient and μ is the chemical potential of adatoms [15,16,18]. This relation may be put down as follows

$$J = -L \frac{\partial \mu}{\partial n} \frac{\partial n}{\partial x}$$

which allows one to introduce the effective diffusion coefficient

$$D = L \frac{\partial \mu}{\partial n}$$

In its turn, the transport coefficient is given by

$$L = Bn$$

where B is the mobility of adatoms which can be related through formula to the self-diffusion coefficient D_i ; the latter characterizes of adatoms in a homogeneous layer:

$$B = D_i / kT$$

Thus, we have

$$D(n) = \frac{D_i(n)}{kT} n \frac{\partial \mu}{\partial n} = D_i(n) \frac{\partial(\mu / kT)}{\partial \ln n}$$

The term $\frac{\partial(\mu / kT)}{\partial \ln n}$ is called the thermodynamic factor (TDF).

At low concentrations ($\theta \ll 1$) and in the absence of interaction, μ is given by

$$\mu = \mu^o + kT \ln \theta$$

where μ^o is the standard chemical potential.

In this case, as one should expect, $\partial(\mu / kT) / \partial \ln \theta = 1$

In Langmuir's layer the interaction of adatoms is also absent, but the restriction $\theta \ll 1$ is not imposed and each adsorption site is assumed to be occupied by a single atom. For this model [21],

$$\mu = \mu^o + kT \ln \frac{\theta}{1-\theta}$$

For interacting adatoms μ can be approximated as [22]

$$\mu = \mu^o + kT \ln \frac{\theta}{1-\theta} - q(\theta)$$

where $q(\theta)$ is the coverage dependent adsorption heat; so

$$\frac{\partial(\mu/kT)}{\partial \ln \theta} = \frac{1}{1-\theta} - \frac{\partial(q/kT)}{\partial \ln \theta}$$

The TDF can also be calculated using experimental data on adsorption isotherms [19]. In particular, if the pressure of the gas in equilibrium with an adlayer is sufficiently low so that ideal gas approximation holds, one obtains

$$\frac{\partial(\mu/kT)}{\partial \ln \theta} = \frac{\partial \ln p}{\partial \ln \theta}$$

It is quite evident that lateral interaction between adatoms affects not only the absolute value of D , but also its temperature dependence. In general, the effective activation energy of surface diffusion in a concentration gradient, which we denote by E_d as before, is not equal to the activation energy of adsorbate self-diffusion E_{di} [19]:

$$E_d = E_{di} + \frac{\partial \ln \theta}{\partial \ln p} \frac{\partial q}{\partial \ln \theta}$$

Here, as given previously, p is the pressure of the gas in equilibrium with the adlayer at a coverage θ . Both derivatives are calculated at $T = \text{const}$. It goes without saying that the lateral interaction changes the value of the pre-exponential factor as well.

The above relations account for the origin of the interrelation between surface diffusion and phase transitions in adsorbed layers; on the one hand, the variation of μ with coverage manifests itself in changes of D and other diffusion parameters and, on the other hand, this variation governs the whole pattern of phase transitions in the adlayer. It should be pointed out, however, that the functional relation between D and $\frac{\partial(\mu/kT)}{\partial \ln \theta}$ is complicated by the coverage dependence of mobility of adatoms (and that of D_i , respectively), because in different phases both the diffusion parameters and even the mechanisms may be different. Furthermore, this problem cannot be solved in terms of a purely thermodynamic treatment; for this purpose one must necessarily proceed to a detailed analysis of proper atomic models.

An Alternate Approach – Random Walks

Another approach to the problem of surface diffusion was proposed by A. Einstein in 1907. This involved modeling the motion of individual particles as random walks in the same way as the motions of gas molecules are modeled.

This approach involves two assumptions :

1. Each individual particle performs a motion which is independent of the motion of all other particles.

2. One and the same particle in different time intervals will be treated as independent processes as long as we imply that these time intervals are not too short.

This approach gives us expressions for the diffusion coefficient. We know now that this is not the same as the one given by the flux approach above. This is instead called the *tracer diffusion coefficient*. In the one-dimensional case, this is given by

$$D_t = \langle x^2 \rangle / 2t$$

A more interesting case is in two dimensions when we can track the actual positions of some particles. In such a scenario, D_t is given by

$$D_t = \lim_{t \rightarrow \infty} \frac{1}{4Nt} \sum_{i=1}^N \langle |\vec{r}_i(t) - \vec{r}_i(0)|^2 \rangle$$

This provides a way of experimentally measuring the tracer diffusion coefficient. Some of the atoms in the collection can be labeled and their paths tracked. (This labeling is typically done by using radioactive isotopes of the atoms involved in the diffusion. Since these have the same chemical properties as the atoms present initially, this technique does not introduce any error)

We briefly mention here another approach to estimating the diffusion coefficient. This involves imagining the diffusion process to involve the presence of a number of transition states which the atoms go through before resting in the quasi-equilibrium position. Using this transition state theory or activated complex theory as it is also called, we get an expression of the form

$$D_t = D_0 e^{-E_d/kT} .$$

This is a very common way in which experiments present data.

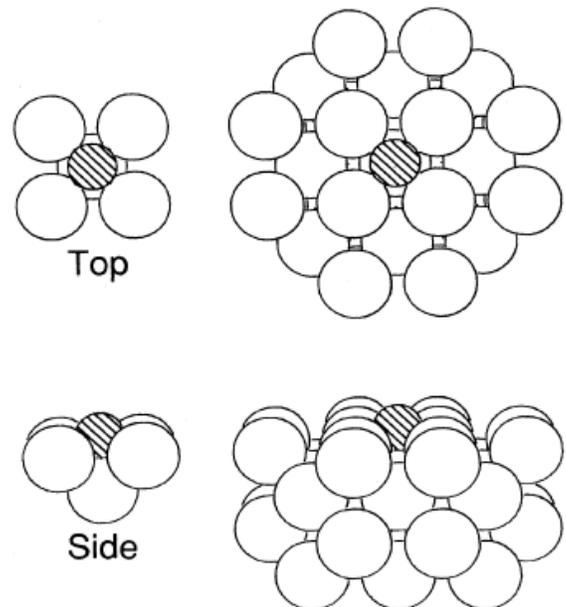
All said and done, it is very important to keep in mind the multi-body nature of surface diffusion. Even at very low concentrations, we cannot possibly ignore this attribute.

Surface Diffusion of Carbon on Fe

Carbon dissolved in transition metals is one of the most important nonmetallic impurities. Carbon is believed to be an interstitial element in cubic lattices and to diffuse through the interstitial sites because it is much smaller than host-metal atoms. We are going to see the properties of carbon diffused on alpha iron. It has been experimentally observed that carbon segregated to metal surfaces is displaced by sulfur at high temperature as expected because the segregation enthalpy of carbon is smaller than that of sulfur. In contrast to Sulfur, carbon is known to enhance the bonding at grain boundaries. Sulfur forms ionic bonds and draws the charge from the metal atoms, leading to weakening of the metal-metal bonds. But carbon forms a covalent Fe $3d$ -C $2s,2p$ interactions with iron there by gets more stabilized.

The ionization potential input parameters for the C $2s$ and $2p$ orbitals are decreased by 1.5 eV from their atomic energy levels because of charge transfer to C. When a C atom is introduced into an interstitial site, not only does its interaction with neighboring Fe atoms affect the energy but also their relaxation around it. Therefore, the energy change, ΔE , can be divided into two parts: ΔE_{Fe} , due to Fe atom relaxation and ΔE_c due to Fe-C bonding. Thus $\Delta E = \Delta E_{Fe} + \Delta E_c$. ΔE_{Fe} should be positive since Fe atoms move away from their equilibrium position toward surrounding Fe atoms of the lattice and ΔE_c is expected to be negative since C binds to its neighboring Fe atoms. ΔE_{Fe} is determined from the comparison of unrelaxed and relaxed systems without C atoms, and ΔE_c comes from subtracting ΔE_{Fe} from ΔE . Since in the ASED-MO theory the total energy is the sum of the two-body repulsion energy, E_R , and the molecular-orbital stabilization energy, E_M , the following formulas can be written: $\Delta E = \Delta E_R + \Delta E_{MO}$, $\Delta E_{Fe} = \Delta E_{R,Fe} + \Delta E_{MO,Fe}$, $\Delta E_c = \Delta E_{R,C} + \Delta E_{MO,C}$. It is assumed that the change in spin polarization of the Fe atoms is induced only by coordination of C to neighboring Fe atoms, not by the relaxation of Fe atoms.

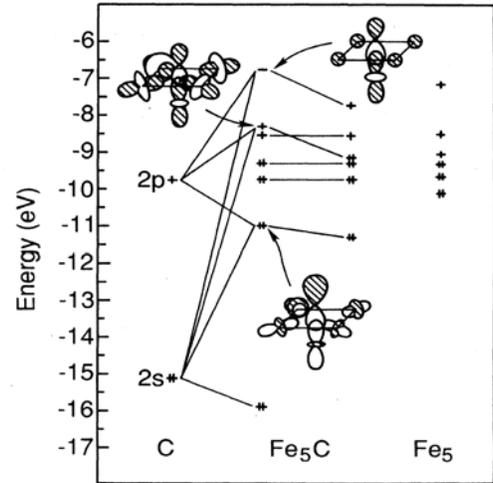
A low-energy electron-diffraction (LEED) study has revealed that C adsorbs at the fourfold sites on Fe(100). The large four-layer Fe₄₂(100) and the smallest Fe₅(100) cluster models were used to study the adsorption of C on the (100) surface. The height of C from the Fe₄₂(100) surface layer is calculated to be 0.64 Å. No experimental value is available but it can be compared with the height of O, which is 0.53±0.06 Å on the Fe(100) surface obtained from LEED analysis. The distance between C and the second-layer Fe



directly below is 2.07 Å, which is shorter than 2.13 Å between C and the surface layer Fe atoms.

The binding energy (BE) of C on the Fe₄₂(100) surface is calculated to be 7.89 eV. This is close to the value of 7.56 eV deduced from the segregation enthalpy and the relative partial enthalpy of carbon in α-iron. No direct measurement is available. When the same height of C is used on the Fe₅(100) surface, the BE is calculated to be 7.23 eV.

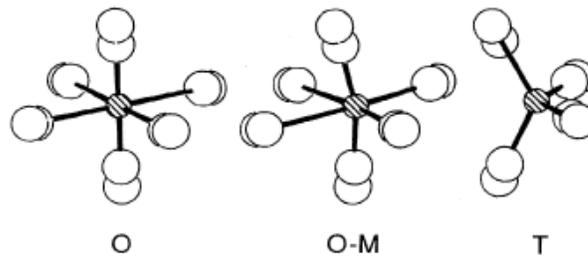
The molecular-orbital diagram for the large Fe₄₂(100)C_{ad} cluster model is expected to be close to the bulk limit for isolated C atom adsorption. For the MO analysis, only the Fe₅(100)C_{ad} cluster is used and the MO diagram for a-symmetry orbital interactions is shown in Fig. The C 2p_z orbital interacts mainly with Fe 3d orbitals and stabilizes them. The C 2s orbital undergoes a bonding stabilization by mixing with Fe 4s + 3d orbitals but also pushes up the stabilized C 2p_z + Fe 3d bonding orbitals by antibonding mixing with the C 2p_z orbital. When the interaction of the C 2s orbital with Fe orbitals is removed by moving down the C 2s level to -50 eV and shrinking the orbital by using a Slater exponent of 30 a.u., the BE of C on the Fe₄₂(100) surface becomes 7.79 eV, which is 0.10 eV, less than when the C 2s orbital interactions is permitted. Consequently, the C 2s orbital interaction with the Fe surface band is bonding, unlike in the S case, though very weak.



C at interstitial sites in α-iron

In bcc α-iron the interstitial C atom has been believed to occupy either an octahedral (O) site or a tetrahedral (T) site and diffuse from one site to the other. The O site has two Fe atoms at a distance of 1.43 Å and four Fe atoms 2.02 Å away from the center. An Fe₅ cluster model was used for studying C at interstitial site.

This enables relaxations of surrounding Fe atoms to be included. The five sites for an interstitial C atom are O, T, one-fourth (O-M), one-half or middle (M), and three

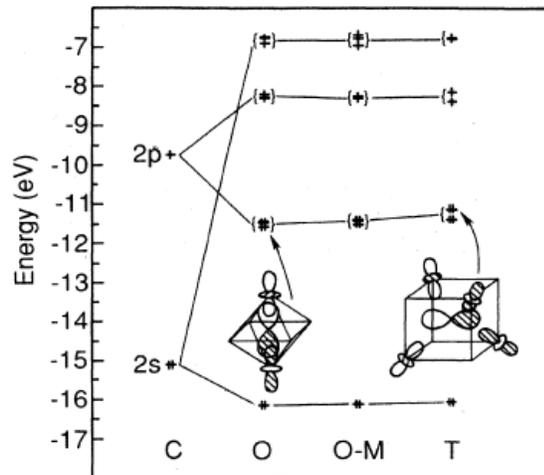


fourths (M-T) of the distance between the O and T sites. The optimized structures for C at the O, T, and O-M sites are shown in Fig. In the O structure, the two nearest-neighbor Fe atoms move away 0.46 Å and the next-nearest four Fe atoms move 0.11 Å away from their original lattice points. The distance between C and the nearest Fe atoms is 1.89 Å and between C and the next nearest ones it is 2.13 Å. In the T structure, four Fe atoms adjacent to C expand by 0.37 Å to a distance of 1.97 Å. Twenty more Fe atoms are relaxed. Eight of them move away 0.18 Å from their original lattice points and the rest of them move 0.04 Å. When C occupies the O-M site, the two Fe atoms at apexes of the O

structure expand 0.47 Å to a distance of 1.91 Å. The two Fe atoms close to C at corners of the square move 0.18 Å away to a distance of 2.09 Å and the other two Fe atoms at corners of the other side also relax 0.12 Å away. The four Fe atoms surrounding the two Fe atoms at the apexes move 0.18 Å. The other four atoms surrounding the two Fe atoms close to C move 0.13 Å. Twelve more surrounding Fe atoms relax < 0.07 Å. The change in energy for C moving from the O site through the T site is shown in the fig. The O and T sites are comparable in energy to each other but both of them are predicted to be less stable than the O-M site. It was found that the sum of $\Delta E_{MO,C}$ and $\Delta E_{R,C}$ is minimum at the O-M site. Also at this site the destabilization due to relaxations of Fe atoms is the least; it is greatest at the O site. As a result, the O-M site turns out to be the most favorable for an interstitial C atom. No conspicuous change in MO levels for the different sites of C can be found except for the C $2p$ + Fe d bonding orbitals. At the T site these levels are less stabilized compared to those at the other two sites. The C $2s$ orbital is greatly stabilized and splits far from its empty antibonding counterparts because of the large overlap resulting from the short Fe-C distance.

The bonding of a C atom to Fe atoms is achieved predominantly through the overlap of C $2p$ orbitals with Fe $4s$ + $3d$ band orbitals irrespective of the position of C in the Fe matrix. The MO energy gain is about 1 eV greater in interstitial sites than on the (100) surface. The result of the C $2s$ orbital interaction with the Fe $4s$ + $3d$ band depends on the position of C; it is almost nonbonding on the surface and weakly bonding at interstitial sites.

Since the C $2s$ orbital induces net bonding character, though very weak on the surface and at interstitial sites of α -iron, there is no closed-shell interaction, as was observed for sulfur. Rather, the interaction of a C atom with surrounding Fe atoms is stronger at interstitial sites than on a surface. Therefore, the driving force for C segregation is not the same as for S segregation. We can notice that ΔE for C on the (100) surface is about the same as ΔE_C for C at interstitial sites. The difference between two states amounts to ΔE_{Fe} , 0.96 eV, which is the destabilization energy of Fe atoms due to the relaxations. Therefore, the driving force for C segregation comes from the Fe-Fe repulsion energy. The strong bonding of C to Fe is achieved through the interaction of C $2p$ orbitals with Fe $4s$ + $3d$ band orbitals. The interaction of the C $2s$ orbital with the Fe $4s$ + $3d$ band is dependent on the position of C in α -iron. On the (100) surface it shows weak bonding and at the interstitial sites slightly stronger bonding. This is in contrast to substitutional sulfur, for which our past study found a significant closed-shell repulsive interaction between the S valence $3s$ orbital and the Fe valence band. For an interstitial C atom in α -iron, it is predicted that the octahedral site is the least favorable and the offoctahedral site one-fourth towards a tetrahedral site is the most favorable. It is deduced from the comparison



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of energy components of C on the (100) surface and in the interstitial site that C atoms segregate to the surface because of the repulsive compression of Fe-Fe bonds surrounding the interstitial C

Experimental techniques used in Surface Diffusion studies

Existing techniques that detect surface diffusion processes can be grouped into two main categories. In the first of them experimentalists observe the processes of equilibration realized via surface diffusion in various nonequilibrium systems (nonequilibrium methods). In the second category of the methods, the systems are in equilibrium. There is no net mass transport on the macroscopic scale in this case, but the particles perform thermal fluctuations around the equilibrium state. These fluctuations are the source of information about the mobility of the particles in such “equilibrium methods”. It is understood that each class of the methods gives evidence on particle mobilities in conditions that can be substantially different. This generally results in difference of the values of the diffusion parameters extracted from the equilibrium and nonequilibrium measurements.

Nonequilibrium methods

The task of such experiments is to record the kinetics of the transition, executed by surface diffusion, from a nonequilibrium state of the object to the equilibrium one. Consider the case of surface self-diffusion. A typical example is the change of the shape of a crystal observed under annealing. Suppose the annealing temperature is low enough to preclude evaporation of the crystal and volume diffusion within it. Then the equilibration, i.e., the minimization of the surface free energy by a shape change, is attained through surface self-diffusion only. For instance, any sharp tip is getting blunter under annealing. Such experiments can be carried out with atomic resolution by field ion microscopy. In some other cases electron microscopy and optical interferometry are also used. The disadvantage of such methods is that their results relate to the surfaces whose atomic structure is changing during the experiment.

The nonequilibrium methods developed to investigate surface diffusion of adsorbates use one or another physical quantity sensitive to adparticle concentration (coverage) on the surface. The measurement of this quantity with an appropriate spatial resolution allows recording the time variation of the adsorbate surface distribution (coverage profile) as the adsorbed layer evolves from a Nonequilibrium initial state to its equilibrium final state (Fig 5). The process of evolution of the coverage profiles can be followed by scanning the surface with such probes as electron, ion and light beams, or a tip in various scanning

probe microscopies. The field emission and photoemission microscopies also are successfully employed to display the adsorbate distributions on the substrates.

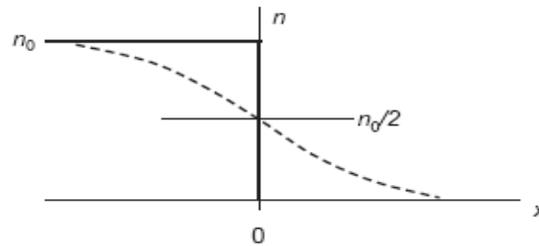


Fig. 5. Concentration profile (dashed line) in the case of diffusion of noninteracting particles from a step-like initial deposit.

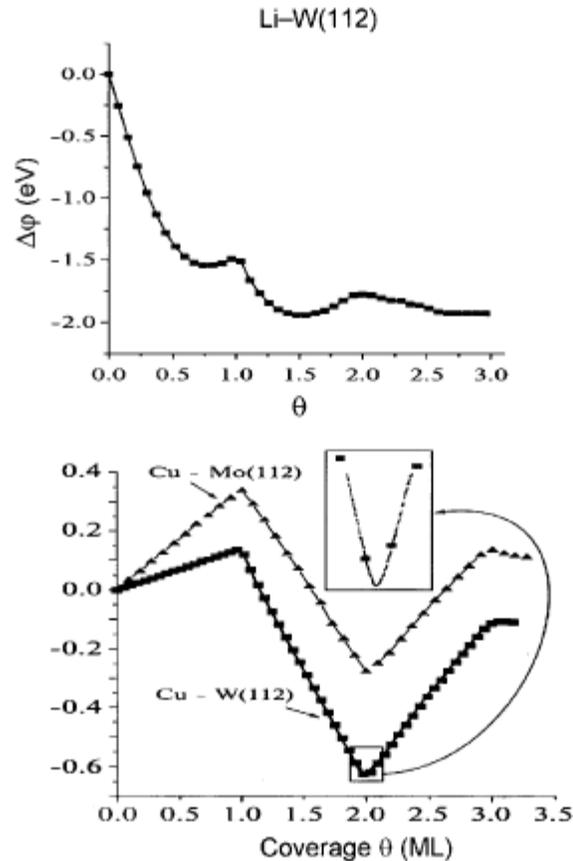
Field-ion and scanning tunneling microscopies provide direct views of individual atoms and molecules on surfaces. Other techniques give data, such as electron or ion currents, work function, intensity of atom or light beams, etc., that must be converted to coverage degree (adsorbate surface concentration). This is accomplished through corresponding calibration procedures that establish the relationship between the adatom concentration and the physical values immediately measured in concrete experiments.

The most important features of the experimental techniques applied to study surface diffusion are their spatial resolution and accuracy of coverage determination.

Spatial resolution:

Field-ion and scanning tunneling microscopies	:	10^{-8} cm
Photoelectron and other types of electron microscopies and scanning contact-potential microscopy.	:	1–10 μ m

Scanning contact-potential microscopy provides an accuracy in coverage determination to about 10^{-2} of a monolayer in the coverage intervals where the work function strongly depends on coverage as shown in figure below



. Work function change $\Delta\phi$ versus coverage θ (in monolayers) for Li and Cu on W and Mo(112)

Field ion microscopy (FIM)

- atomic resolution possible
- very efficient in following surface diffusion of single atoms and small clusters (oligomers)
- Only applicable to materials which can withstand high electric fields of 10^8 V/cm.
- The small size of the crystal planes on sharp tips used in field ion microscopes makes impracticable quantitative recording of the evolution of coverage profiles and investigations of phase effects in surface diffusion.

Surface Tunneling Microscopy

- 2 Visualization possible
- 3 But rather high electric fields under the tip and the high-density tunneling current can sometimes induce a specific mobility of the adparticles

The much more modest resolution of such methods as photoelectron microscopy and scanning contact-potential microscopy (1–10 nm) is rewarded with a high accuracy of coverage determination, nondestructive character of the measurements and the possibility to observe phase effects in surface diffusion over rather large distances.

Equilibrium methods

Field Ion Microscopy

In FIM, a sharp (<50 nm tip radius) metal tip is produced and placed in an ultra high vacuum chamber, which is backfilled with an imaging gas such as helium or neon. The tip is cooled to cryogenic temperatures (20–100 K). A positive voltage of 5000 to 10 000 volts is applied to the tip. Gas atoms adsorbed on the tip are ionized by the strong electric field in the vicinity of the tip (thus, "field ionization"), becoming positively charged and being repelled from the tip. The curvature of the surface near the tip causes a natural magnification — ions are repelled in a direction roughly perpendicular to the surface (a "point projection" effect). A detector is placed so as to collect these repelled ions; the image formed from all the collected ions can be of sufficient resolution to image individual atoms on the tip surface.

Field emission microscopy (FEM) and STM are two versions of method of surface diffusion investigation based on recording thermal density fluctuations in adsorbed layers.

FEM fluctuation technique

FEM consists of a sharp needle emitter and a detector, such as a fluorescent screen. A negative electric field is applied to the emitter, emitting electrons from the surface. An image is formed at the detector due to the different current densities, which originates from the difference in electric fields and work functions on the emitter surface by the Fowler-Nordheim equation.

The original physical quantity recorded in this technique is the field emission current collected from a small ($\leq 100 \text{ \AA}^2$ in size) surface area. The current fluctuations stem mainly from the fluctuations of the number of adatoms within the probed area, which cause local work function variations. In turn, the density fluctuations in the adlayer can only occur thanks to the existence of a mobility of adatoms. Thus, the investigation of the process of building-up and decay of the adatom density fluctuations gives a possibility to extract the diffusion coefficient from the autocorrelation function of the fluctuations.

STM fluctuation technique

In this method, one records the fluctuations of the tunneling current caused by passing the diffusing particles under an immobile tip.

Inelastic Helium atom scattering

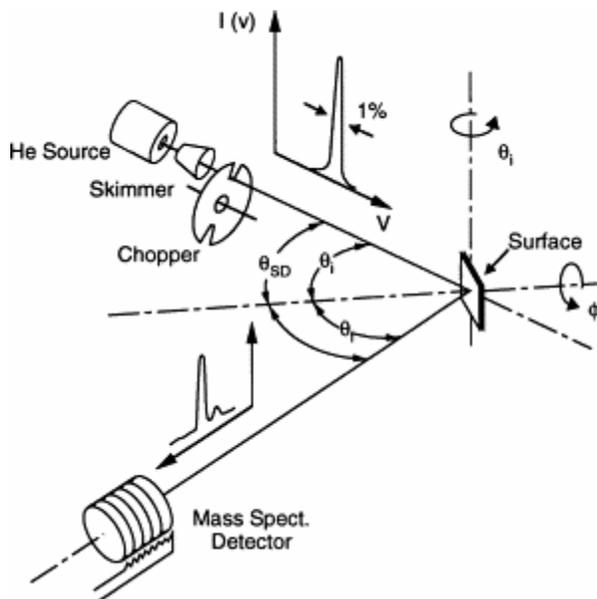
Over two decades ago, inelastic helium atom scattering (HAS) was developed into a high resolution method to probe the low frequency dynamics of both clean and adsorbate covered surfaces. High resolution helium atom scattering (HAS) has proved to be a useful probe of the low frequency (<20 meV, <160 cm^{-1}) dynamics of adsorbates on metal surfaces including diffusion.

Thermal energy of helium atoms ($E_i=4\text{--}100$ meV, $30\text{--}800$ cm^{-1}) have the following advantage over other probe particles, such as electrons and photons

- They do not penetrate the surface but, instead, turn away $3\text{--}4$ Å from the surface where the electron density is low (10^{-4} $\text{e}\text{\AA}^{-3}$)
- Can be generated with very narrow velocity distributions using supersonic expansion, typically $\Delta v/v < 1\%$, permitting resolutions in the low sub-meV range. This resolution, combined with the large cross-section for scattering from molecules, makes HAS a very useful and, in some cases, the only probe of low frequency surface dynamics.
- Low adsorption energy of helium on surfaces coupled with the chemical inertness of helium atoms ensures that the beam itself does not alter the surface

The HAS Experiment:

Diagram showing the essential details of a fixed total scattering angle HAS apparatus. Helium expanding from the high pressure nozzle is collimated and chopped into short bursts. The helium pulses scattered from the surface through a fixed total scattering angle θ_{SD} are detected by a helium specific detector in a TOF mode. The flight times can then be converted into energy transfer to the surface during the collision. The momentum transfer parallel to the surface $\hbar\Delta K$ is varied by changing the incident angle of the helium atom beam to the surface.



(7K)

Decay-detected nuclear magnetic resonance

-measures the spin-lattice relaxation rate

The low energy dynamics of adsorbates on metal surfaces investigated with helium atom scattering Andrew P. Graham Science direct Volume 49, Issues 4-5 , April 2003, Pages 115-168

Effect of defects on surface

In order to gain insight into essential physics of this impact of defects on surface diffusion, experimentalists must work with surfaces that possess controllable (intentionally created and well characterized) defect.

The point-like defects such as vacancies, single impurity atoms, etc. act as traps (attracting sites) or antitraps (repulsing sites) for diffusing particles. A trap can be filled by a diffusing atom which then may either attract or repulse the other diffusing atoms. In the former case the trap acts as a nucleation center if the temperature and the adatom density correspond to the region of a first-order phase transition in the diffusing overlayer. In contrast, if the point-like defect (either empty or filled) is a repulsive center, the other diffusing atoms will bypass it.

In the particular case when surface potential corrugation is strongly anisotropic and the diffusion predominantly proceeds along the atomic troughs (channels), the point-like defects situated within the channels can dramatically block the diffusion. A similar strong suppression of surface diffusion by point-like defects is observed in the case of soliton diffusion mechanism. This mechanism has a pronounced collective character: the mass transport is affected by solitons, which represent linear many-particle objects (domain walls) and can be effectively pinned by point-like defects. Linear surface defects such as atomic steps and grain boundaries can have a strong impact on surface diffusion, because the diffusing particles cannot bypass them.

Broadly speaking, diffusion on surface with defects presents a particular case of diffusion in (for our situation, on) disordered media. This is a complicated theoretical problem which is approached by involving such concepts as a certain hierarchy of defects according to their scale, percolation; possible fractal structure of the medium, etc. The diffusion in (on) disordered media differs by some unusual features. For example, the mean-square displacement of the diffusing particles increases in this case nonlinearly versus time. This gave grounds to term such diffusion anomalous in contrast to normal diffusion where (on defect-free surfaces) one has $\langle x^2 \rangle \propto t$.

Applications of Surface Diffusion

Applications in Nano-Technology

The surface diffusion of large organic molecules on solid surfaces has attracted considerable attention in recent years, partly from the point of view of basic science, partly because of the potential applications in emerging nanotechnological fields, such as molecular electronics, optoelectronics or nanomechanical sensors. In general, molecular assembly will be controlled both by thermodynamic factors—the molecules tend to assemble on surfaces into the energetically most stable structures; and by kinetic factors—the molecules diffuse and interact at surfaces, thereby creating metastable molecular nanostructures that may hinder the molecules at a given temperature from attaining the minimum energy arrangement. A nanoscale understanding of the complex dynamics of large molecules at surfaces is essential for the bottom-up design of molecular nanostructures. It has been shown that the diffusion coefficient of the complex organic molecule known as Violet Lander (VL, C₁₀₈H₁₀₄) on Cu(110) can be changed by two orders of magnitude by using the STM at low temperatures to switch between two adsorption configurations that differ only in the molecular orientation with respect to the substrate lattice.

Otero et al. made a remarkable breakthrough a few years back when they showed that orientation and shape of large and complex organic molecules influence their surface diffusion dynamics. They showed that the diffusion coefficient of the complex organic molecule known as the Violet Lander (VL, C₁₀₈H₁₀₄) on a Cu (110) surface can be changed by two orders of magnitude by deliberately manipulating the VL molecules to change their orientation with respect to the substrate. Combining the results with molecular dynamics simulations, we show that the experimental findings can be attributed to the different registries between the molecule and the substrate for the different molecular orientations. An orientation dependence of the molecular diffusion coefficient plays a significant role in controlling the molecular assembly of large organic molecules whose shape allows them to adopt different adsorption orientations and, thus, different registries with the substrate.

The Violet Lander molecule consists of a polyaromatic π -system (molecular board) with four 3, 5-di-*t*-butylphenyl substituents σ -bonded to the central board; the so-called ‘spacer legs’. On deposition onto a Cu(110) surface the molecules appear in STM images as entities with four protrusions corresponding to high electron tunneling probability through the spacer legs into the substrate. To explore the energy landscape for the VL molecule on the Cu(110) surface Otero et al, used the STM tip as a tool to push the molecule gently in a direction perpendicular to the board of the molecules, thereby manipulating the orientation of individual molecules at low temperatures (160–200 K). This procedure results in a rotation of the molecular board by 70° with respect to the close packed direction of the Cu substrate in about 60% of the cases.

When the molecules are manipulated on a flat terrace they can be forced into no other orientations. The rotated configuration can only be observed at temperatures below 200 K, and in this range of temperatures they do not spontaneously switch to the non-rotated configuration. They are thus trapped in a metastable state that is kinetically stabilized at low temperatures. No significant conformational change of the molecules was found to occur during the manipulation process.

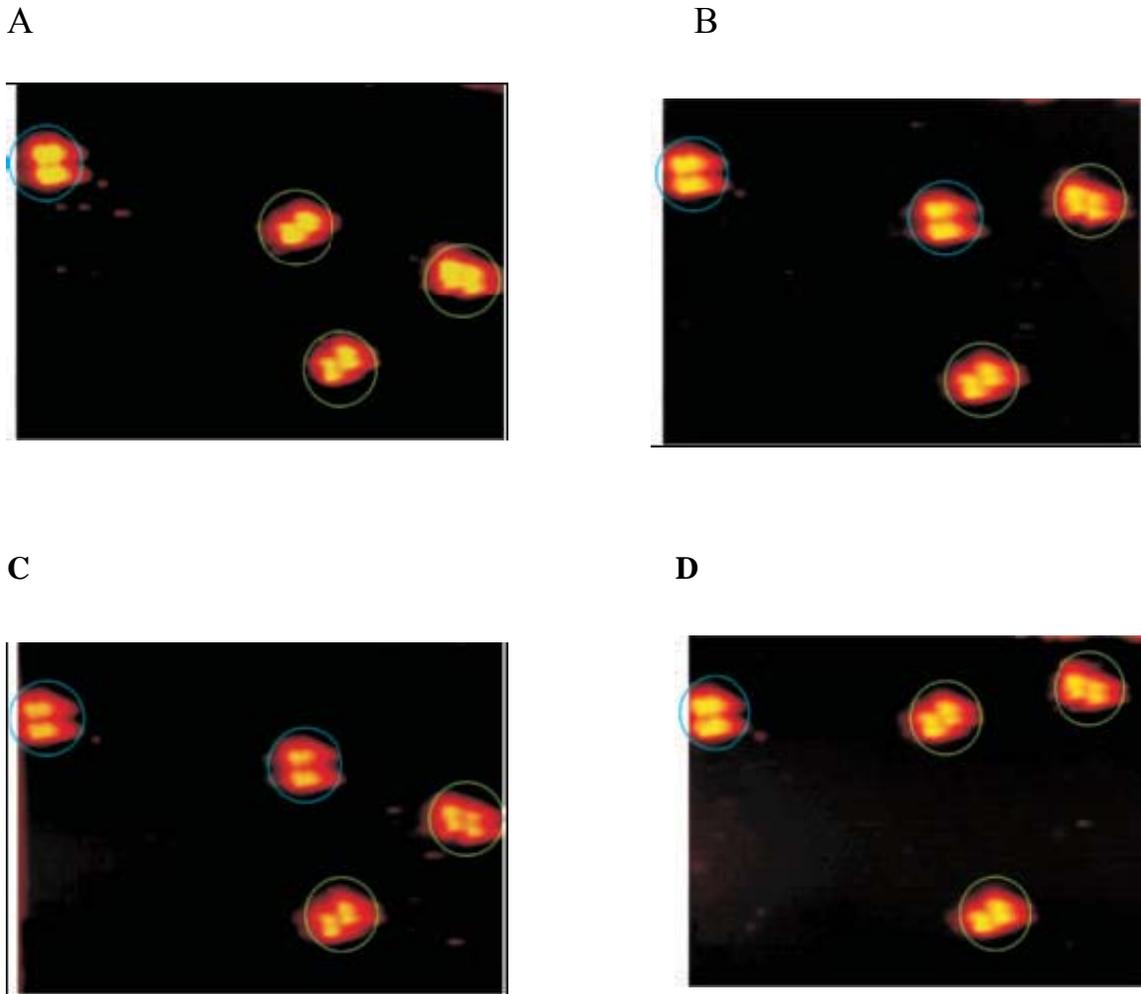


Fig: Snapshots of STM movie recorded at 180 K. The field of view is $28 \times 20 \text{ m}^2$. Before the movie is started, two molecules have been rotated with the STM tip (green circles). Another two molecules are aligned along $[11-0]$ (blue circles). Between A and B only the rotated molecules diffuse, whereas the non-rotated molecules remain in place. However, when molecule 1 is rotated 70° , as happens between the stills B and C, it also starts diffusing (D).

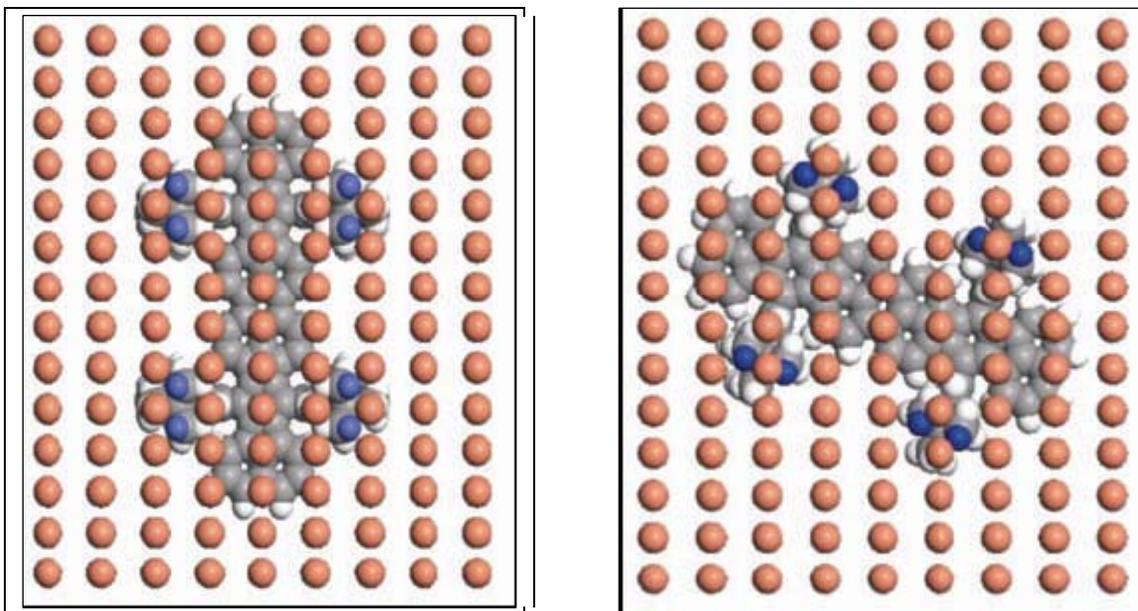


Fig: Bottom views of the adsorbed VL molecule and first Cu layer, showing the different registries between the contact H atoms and the fourfold hollow site for the non-rotated and rotated molecules.

From the STM movies the molecular diffusion coefficient can be determined by tracking the position of the individual molecules. Surprisingly it was found that, whereas the manipulated molecules in the rotated configuration are found to diffuse along the direction with a diffusion coefficient of $D = (4.8 \pm 0.5) \times 10^{-17} \text{ cm}^2 \text{ s}^{-1}$, the molecules in the parallel configuration do not change their relative positions in the time span of the STM movies (several minutes), corresponding to a diffusion coefficient of less than $5 \times 10^{-19} \text{ cm}^2 \text{ s}^{-1}$. They thus concluded that the diffusion coefficient increases by at least two orders of magnitude when the molecular orientation changes from being aligned parallel to the closed-packed direction of the Cu (110) surface to being rotated by 70° .

Although the molecule was immobile before the manipulation, once its board is rotated, it is observed to diffuse with the same diffusion constant as other rotated molecules. Similarly, the molecular diffusion can be stopped at any time simply by flipping the molecule back to its original parallel configuration. The diffusion of the individual VL molecules can thus be activated or deactivated by STM-induced molecular rotations with respect to the close-packed direction of the Cu (110) surface.

These results can be intuitively understood by considering the extent to which the 3D VL shape fits the atomic lattice of the Cu (110) substrate. The VL molecule adsorbed on the Cu substrate exposes eight hydrogen atoms at the bottom of the legs that provide the closest contact between the surface and the molecule. In the non-rotated geometry, these H atoms are in perfect registry with the fourfold hollow sites of Cu (110): the molecular shape fits the atomic lattice of the substrate (Fig. 3b). Any displacement of the molecule's centre of mass results in a less good fit between the H atoms and the fourfold hollow sites of the Cu (110) surface.

For the rotated molecules, however, the registry between the H atoms and the fourfold hollow sites of the substrate is not as good: the molecular shape no longer fits the atomic registry of the substrate template. In this case, mechanical excitations would be expected to result in molecular displacements, because a displacement of the centre of mass does not significantly alter the registry between the H atoms and the fourfold hollow site.

The dynamics of large organic molecules on surfaces is, therefore, analogous to the dynamics of the so-called lock-and-key recognition between enzymes and the substrate on which they act. In the case of enzymes, this binding takes place only when the binding geometry of the substrate (key) makes an exact fit to the enzyme's active site (lock): any other binding geometry would decrease the fit between the enzyme and the substrate, thereby decreasing the binding energy.

This alternative binding geometry can thus be considered as a metastable state that will either decay into the correct binding geometry, provided that there are no kinetic limitations, or lead to a dissociation of the dimer, and the substrate molecule would eventually be released and drift away from the active centre. In the case of the VL molecules, when deposited at high temperature (no kinetic stabilization of metastable states) all VL molecules are oriented parallel to the close-packed direction in such a way that their shape fits the atomic lattice of the Cu (110) surface (lock). A metastable configuration, in which the molecules are rotated and therefore do not fit the Cu (110) substrate, can be forced with the STM tip and stabilized at low temperatures. The interaction between the substrate and the rotated molecules is markedly decreased by the lack of registry with the substrate template and the molecules thus move from their adsorption sites, that is, diffuse on the surface.

The results obtained by Otero et al. indicate that the mechanical stability of complex molecular species on solid surfaces depends strongly on the complementarity between the molecular 3D shape and the atomic registry of the substrate. Molecules with a shape that fits the atomic lattice of the substrate have a very low diffusivity and therefore such molecular nanostructures are stable for longer time spans. The results are thus of great relevance to the emerging area of nanotechnology in which functional molecular nanostructures are built in a bottom-up approach.

1) Catalysis:

We use chemical vapor deposition (CVD) for making nanoscale materials such as carbon nanotubes (CNTs) and carbon nanofibers (CNFs). In CVD we require low temperature so as to enable the use of more sensitive substrates or integration processes. We can study two types of CVD to see the importance of surface diffusion regarding this aspect

a) In thermal CVD activation energy has to be equal to dissociation of gas phase C_2H_2 or CH_4 which produces C atom for diffusion on or in the catalyst.

b) In Plasma enhanced CVD (PECVD) the rate limiting step is carbon diffusion on catalyst surface which lowers the activation energy .Hence we can have lower temperature.

2) Soldering:

The surface diffusion is the mechanism responsible for the transport of Sn inside the solder joint. It also causes the Sn transport rate at locations near the surface to be higher than those in the interior of solder joints. Surface diffusion also accelerates the homogenization process of the solder joints.

Mostly Sn-Pb alloy is used but due to environmental concerns arising from the toxicity of Pb, several other solders such as Sn-Ag, Sn-Cu alloys, have been considered to replace Sn-Pb solders. Proper understanding of surface diffusion parameters such as which species will dominate diffusion is necessary as it governs wetting, joint strength and reliability.

3) Surface diffusion in nanotechnology:

In nanopatterning, surface diffusion is the mechanism involved. To illustrate we see the following example

We concentrate on Co growth on strained thin Pt films. We can have a pattern of vertical pillars fabricated by self-assembly and self-organization on the surface. Here for example a thin film of Pt can be deposited on the clean flat surface of sapphire. Due to the mismatch of the lattice constants, dislocations evolve in the Pt film when it is relaxed. These dislocations repel each other so that the equilibrium configuration is given by an equally spaced dislocation array. So we have a well defined array. During patterning process Co atoms get diffused on Pt atoms and will start nucleating. Here it was observed that diffusion increases with tensile strain showing that preferred nucleation occurs in the regions of high tensile stress. Hence in the end we get desired pattern.

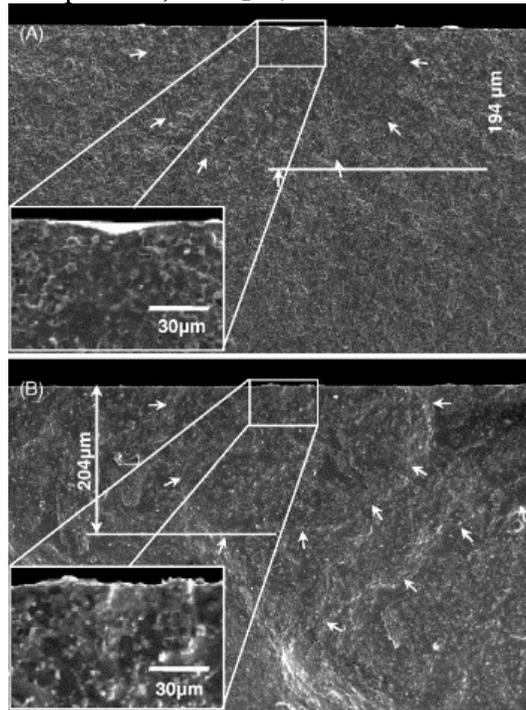
4) Power Metallurgy:

In power metallurgy also surface diffusion plays an important role. There are three steps in power metallurgy

- d) **Mixing:** Metal powders are first mixed with lubricants or other alloy additions to produce a homogeneous mixture of ingredients.
- e) **Compacting:** A controlled amount of mixed powder is compacted at high pressures .Compacting the loose powder produces a "green compact", which has the size and shape of the finished part and sufficient strength for in-process handling and transport to a sintering furnace.
- f) **Sintering:** Here the "green compact", is placed on a wide-mesh belt, and is slowly moved through a controlled-atmosphere furnace. Parts are heated to below the melting point of the base metal, held at the sintering temperature, and then cooled. Since we have through high-temperature treatment and sintering of powder compacts has no liquid phase. Here predominant mass transport (i.e. densification mechanism) is solid-state diffusion. We have a reduction of compact porosity. .So due to surface diffusion we do not have shrinkage in volume but formation of

solid bonds between adjacent particle. This results in sintered material having better mechanical properties like better strength and toughness etc.

5) Repairing: The mechanism of surface diffusion can be used for repairing of defects. For example as in oxidation of NiO with the matrix- Al_2O_3 , the rapid diffusion along with the grain boundary repairs damages on the surface by filling and re-bonding the defects and cracks with the reaction product, NiAl_2O_4 .



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