Surface Engineering for Corrosion and Wear Resistance Application

Prof. Indranil Manna
Department of Metallurgical and Materials Engineering
Indian Institute of Technology, Kharagpur

Lecture - 04
Surface and Surface Energy

Welcome to the 4th lecture of this series on Surface Engineering. We are still discussing the fundamentals of solids before we enter into the elaborate discussion on various kinds of surface properties and processes that are considered as surface engineering.

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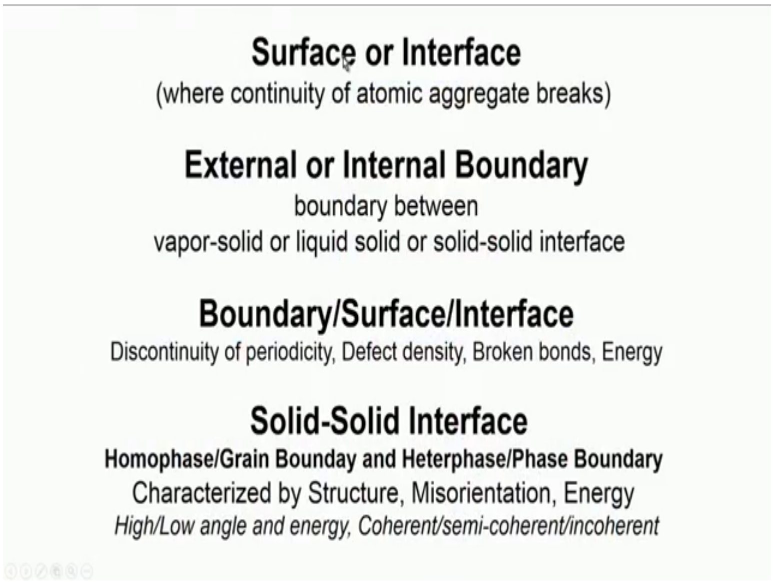

Surface or Interface
(where continuity of atomic aggregate breaks)

External or Internal Boundary
boundary between
vapor-solid or liquid solid or solid-solid interface

Boundary/Surface/Interface
Discontinuity of periodicity, Defect density, Broken bonds, Energy

Solid-Solid Interface
Homophase/Grain Bounday and Heterphase/Phase Boundary
Characterized by Structure, Misorientation, Energy
High/Low angle and energy, Coherent/semi-coherent/incoherent

In the last lecture we talked about defects in crystals so, what we realize that dimensionally one can have various kinds of defects. In this particular lecture we are going to talk or essentially discuss the reason why surfaces arise the genesis of surface energy and how does surface energy or various structures and properties of surface affect the overall performance of any solid. In fact, a whole courses on surface engineering.

So, we must understand what do we mean by surface; now, surface essentially is an entity where the continuity of the aggregate breaks down or ends. Now if you imagine a set of atoms which either are manifesting in the form of a crystals or crystalline aggregate where we have three-dimensional periodicity or if you can have a situation where you do not have two-dimensional periodicity. So, be it crystalline or amorphous in either cases will have a situation where a certain continuity gets broken down or ends at a particular site. So, wherever such continuity ends we create a surface.

So, for that matter if you take any solid, you will always you can always imagine that the solid no matter what you have inside, certainly has an outer contour and that is where it actually interfaces with surrounding or with the atmosphere. So, we can have such a surface, we can have such a situation where the continuity breaks down onto the external surface. But such surfaces can exist even inside the solid which we do not get to see by naked eye because we have the solid in all probability is an opaque solid, but if it is a transparent solid you may actually discover that there are interfaces within.

So, in general let us say surface is essentially a situation where the atomic or ionic or molecular aggregate ends its continuity and this kind of situation where the continuity breaks down can happen either at the external surface which is the solid vapour interface or within the boundary; within the bulk of the solid and which we call internal boundary. So, the boundary is essentially either vapour solid or solid liquid or solid solid are all qualified to be called as external or internal boundaries. In fact, you can have for a situation where the two vapour phases are immiscible or if we have a situation where two liquids are immiscible; there also you can have interfaces.

But since we are talking about solid surfaces here so, we essentially should concentrate on solid vapour interfaces which is the external interface or solid liquid interface which also could be an external interface in a situation; for example, when a solid is growing out of a liquid or in most of the other cases we have solid solid interfaces which are called internal boundaries.

So, boundaries surfaces or interfaces they essentially allude to the fact that there is a discontinuity of periodicity they there is likelihood of having certain density of defects. We certainly have and bonds because we do not maintain the same surrounding as we can have inside or in the interior of the crystal. And as a result of these broken bonds, we certainly can imagine that there should be existence of an energy component which is different than that of inside the bulk.

Now talking about the solid solid interfaces which is what is very very important for defining all the properties of solids that we see, they can be of two types either the so, called homo-phase or grain boundary or hetero phase or phase boundary. What it means is that if the if the entities across a particular boundary are having the same crystal structure and same composition only differing in orientation then we simply call it grain boundary or homophase boundary.

On the other hand if you have a situation where the two entities across the boundary differ in crystal structure, differ in composition then we call it a phase boundary or interface-interface or hetero phase a boundary. Now, all the boundaries whether it is a grain or phase boundary, they can be characterized in terms of their structure, boundaries also do have their own structure. And primarily containing certain amount of defects the boundaries are characterized by misorientation or the angle of misorientation between the two crystallites, and certainly in terms of the energy they carry.

So, as a in taking cue from these kind of basis for differentiation or classification, we can have high angle and low angle boundary where the usually the inner the angle of misorientation is below when it is below of few degrees, we call it low angle when it is several degrees then we call it high angle boundaries. And these boundaries actually can be either the tilt-boundaries and that is where you actually can easily explain the energy explain the misorientation angles.

You can also characterize the boundaries in terms of energy and you can also explain in terms of the coherency or the structural match across the boundary and call them coherent, semi-coherent or incoherent boundaries.

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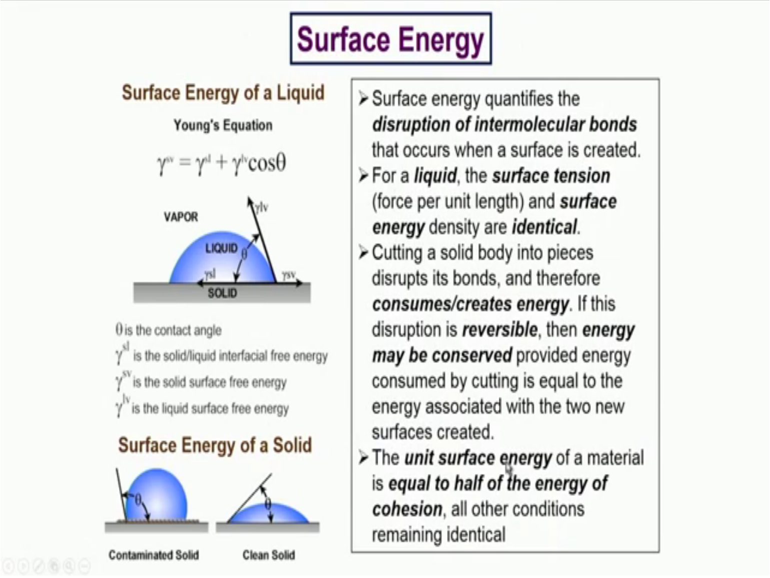

Surface Energy

Surface Energy of a Liquid

Young's Equation

$$\gamma^{sv} = \gamma^{sl} + \gamma^{lv}\cos\theta$$

θ is the contact angle

γ^{sl} is the solid/liquid interfacial free energy

γ^{sv} is the solid surface free energy

γ^{lv} is the liquid surface free energy

Surface Energy of a Solid

- Surface energy quantifies the ***disruption of intermolecular bonds*** that occurs when a surface is created.
- For a ***liquid***, the ***surface tension*** (force per unit length) and ***surface energy*** density are ***identical***.
- Cutting a solid body into pieces disrupts its bonds, and therefore ***consumes/creates energy***. If this disruption is ***reversible***, then ***energy may be conserved*** provided energy consumed by cutting is equal to the energy associated with the two new surfaces created.
- The ***unit surface energy*** of a material is ***equal to half of the energy of cohesion***, all other conditions remaining identical

Now, as I said that surface is the position where the continuity breaks down; and as the continuity breaks down so, if you consider an atom sitting in the middle of a crystal and an atom located on to the surface; then the surface atom certainly have will enjoy at least one extra degree of freedom. Which means that the atom in the center will be pushed and pulled by all that atoms surrounding it; that means, its pushed and pulled from all sides. Whereas, that one at the surface will have such attractions and repulsions from all around except from the top or the bottom.

And as a result there will be certain bonds which are not matched by the counterparts from the top or the bottom. And hence these broken bonds will actually the cumulative effect of them will actually be manifested in the form of what is known as surface energy. If you just compare two possible situations that when you allow a drop of ink to fall on a blotting paper think immediately spreads. On the other hand if you imagine a drop of oil placed on top of a glass slide, then you imagine easily can imagine that this drop is not going to spread as easily as you have seen in case of ink on a blotting paper.

So, this is because of structural differences though, but this could be a good analogy to explain what is known as wettability. So, in situations where the liquid spreads very easily over the surface, we say that the liquid has very good wettability onto the surface and the angle of angle subtended will be very small. Now, before that let us first understand what is this wetting angle, that we are talking about or the contact angle that we are talking about.

So, when you imagine a liquid droplet sitting on a solid, you actually can imagine three kinds of interfaces; the solid vapour interfaces which exists even without the presence of this liquid, the liquid vapour interface which is between this surrounding atmosphere and the liquid, and a solid liquid interface which is purely between this droplet and the solid underneath.

So, these three tensors actually are the forces will come to a balance; will come to an equilibrium and that will define or explain what would be the shape that this liquid will take up. If it spreads very easily then this angle is very low and we say that wettability is very high, if it does not wet at all then this angle can be close to 180 degree and that is when we say that this is a non-wetting type.

So, in an clean solid for example, here you see that possibly the liquid can wet very easily and we have a very shallow angle. On the other hand, if we have a situation where the surface area is very high and this because of which the wetting, wetting is very poor and as a result we see a very large contact angle.

So, the surface energy essentially quantifies the disruption that happens disruption of the intermolecular or intermolecular bonds onto the surface and this for a liquid allows us to equate between the surface tension and the surface energy. So, surface tension is force per unit length and surface energies energy per unit area. So, they will be numerically equal if we are talking about a liquid.

Now, as I was trying to explain that if you actually cut across a solid then you create a disruption, and across the section you actually realize that you have unsaturated bonds and the cumulative effect of these unsaturated bonds give rise to what is known as surface or interfacial energy. And if the sectioning is reversible in nature then we may say that the energy is; and also we assume that the energy is conserved then we know exactly that the energy at the surface will be exactly half the energy of the quasi forces existing otherwise, among these atoms across the section. So, this is how the surface energy can be defined or related to the energy of cohesion that exists inside the crystal.

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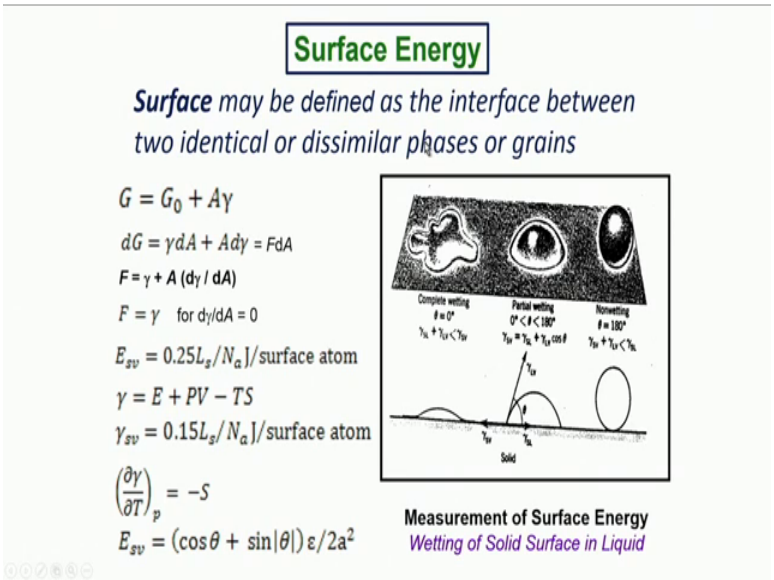

Surface Energy

Surface *may be defined as the interface between two identical or dissimilar phases or grains*

$G = G_0 + A\gamma$

$dG = \gamma dA + A d\gamma = FdA$

$F = \gamma + A\,(d\gamma / dA)$

$F = \gamma$ for $d\gamma/dA = 0$

$E_{sv} = 0.25 L_s / N_a$ J/surface atom

$\gamma = E + PV - TS$

$\gamma_{sv} = 0.15 L_s / N_a$ J/surface atom

$\left(\frac{\partial \gamma}{\partial T}\right)_p = -S$

$E_{sv} = (\cos\theta + \sin|\theta|)\,\varepsilon / 2a^2$

Measurement of Surface Energy

Wetting of Solid Surface in Liquid

So, we have already defined that surface is essentially the interface between two identical or dissimilar phases or grains. So, when they are identical we call them grain boundaries, when they are dissimilar we call them phase boundary and for any normal solid we always will have a solid vapour interface which also is too similar in nature.

So, a Gibbs energy which we know very well is an index of stability of the system, but this is in absolute terms. So, a Gibbs energy of a system which contains not only the bulk, but also the surfaces will have a bulk component. The ideal Gibbs energy and along with that will be an interfacial component which is nothing but, a times gamma where a is the surface area per unit volume and gamma is the surface energy.

Now, the Gibbs energy when you differentiate can also be equated to the force times the incremental increase in area. So, when you actually create a crystal or when you create a surface, then the work that you do actually can be also or the then we also had Gibbs energy component associated with the creation of the surface. And; so, these kind of mathematical treatments actually allow you to understand that the force that exists on to the surface will be equal to the energy surface energy when the variation of surface energy with area is 0. So, this is a typical isotropic situations.

But in general, the surface energy will have an internal energy associated with it and the differences coming from the PV terms; the pressure times volume minus the temperature times entropy. So, this will define the overall energy associated with the surface. But, in plain terms we actually must realize that the surface energy or so called interfacial energy is an important quantity for us to understand the behaviour of solids because this is how it defines; so, for example, in a situation where incoming droplet does not wet at all.

So, we now realize that the wetted wetting angle or the contact angle is practically 180 degree, because there is a there is only a point contact between the droplet and the solid underneath. So, in a situation like this the solid will not get wetted by any incoming for example, such incoming droplets. Now, this could be a very nice example for the solar panels which we see these days on the rooftops which harvest solar energy and convert it into electrical energy. This is a welcome situation on such solar panels because then the panel will not collect dust and other particles and get covered and eventually that could lead to attenuation in the amount of solar energy that you can harvest.

So, in cases where one wants a non-wetting surface or a so called hydrophobic surface, we will go for a situation where by the theta the contact angle could be as close to 180 degree as possible. On the other hand, we actually may require for certain reactivity, certain transformations or certain other purpose a situation where the incoming liquid should wet completely; so, that the wetting angle is 0 degree.

So, for changing the behaviour of a surface from completely hydrophilic to completely hydrophobic one can actually look into the surface morphology, the surface structure and most importantly at surface energy. So, that such characteristics can be obtained and this is how surface actually also dictates whether a certain reaction can happen easily or otherwise on to a particular surface. And when we talk of situations like a mechanical interaction between two solid surfaces or mechanically or electrochemical or chemical interactions, then this kind of surface characteristics and behaviours are very very important.

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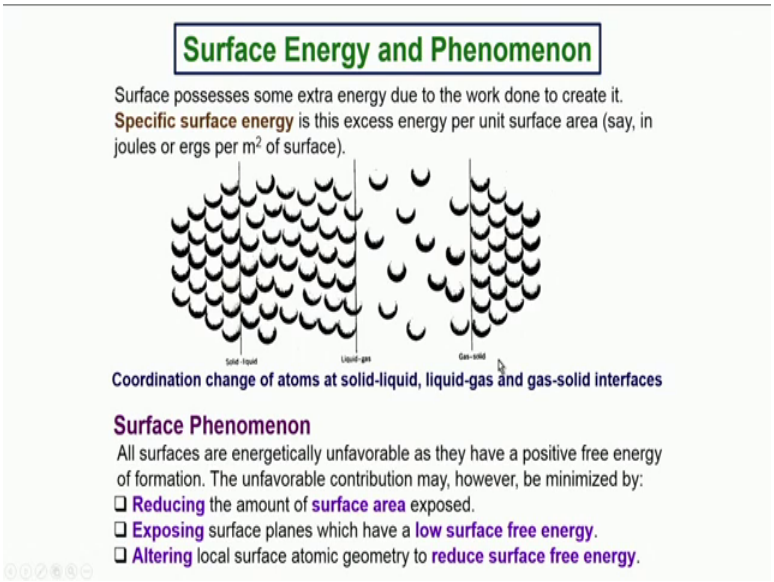

Surface Energy and Phenomenon

Surface possesses some extra energy due to the work done to create it. **Specific surface energy** is this excess energy per unit surface area (say, in joules or ergs per m^2 of surface).

Coordination change of atoms at solid-liquid, liquid-gas and gas-solid interfaces

Surface Phenomenon

All surfaces are energetically unfavorable as they have a positive free energy of formation. The unfavorable contribution may, however, be minimized by:

- ☐ **Reducing** the amount of **surface area** exposed.
- ☐ **Exposing** surface planes which have a **low surface free energy**.
- ☐ **Altering** local surface atomic geometry to **reduce surface free energy**.

Now, typically if you look at these cartoons here you can easily imagine what could be what would it look like an interface between a solid and a liquid. Say for example, this is the liquid where we have a slightly lesser coordination number and wider distance of separation among the species. So, a solid is certainly a denser and has a rigid volume. Liquid does not have a fixed has a fixed volume, but does not have a fixed shape is not rigid and gaseous substances; obviously, is much more free to move around. So obviously, the least dense and the distance between the atoms or molecules would be the largest.

So obviously, whenever you have a solid liquid interface or a solid vapour interface, you do see that there is a difference in atomic configurations across and this is why we actually see all the manifestations of surface related phenomena. Now talking about the surface phenomena we realized that every surface carries a certain amount of energy and that is responsible for a certain behaviour.

So, in order to reduce the surface energy you can do one of the three possibilities, you can reduce the surface area because the overall surface energy, the cumulative term is gamma times a if you reduce a or surface area the overall delta g gamma or the surface energy associated is reduced.

You can choose certain crystallographic planes which actually have low energy or in other words densely packed. So, if you expose those crystallographic planes on to the free surface, then the overall energy of the interface of the surface can be lower or you can actually change the atomic geometry of the surface in order to reuse the surface free energy.

So, when we need to tailor the surface, we must remember that we may need to change the structure or to be more precise the microstructure of the surface, as a result of which the energy can be reduced or changed. And such change of surface energy is also possible by way of segregation or changing the chemistry in the near surface region.

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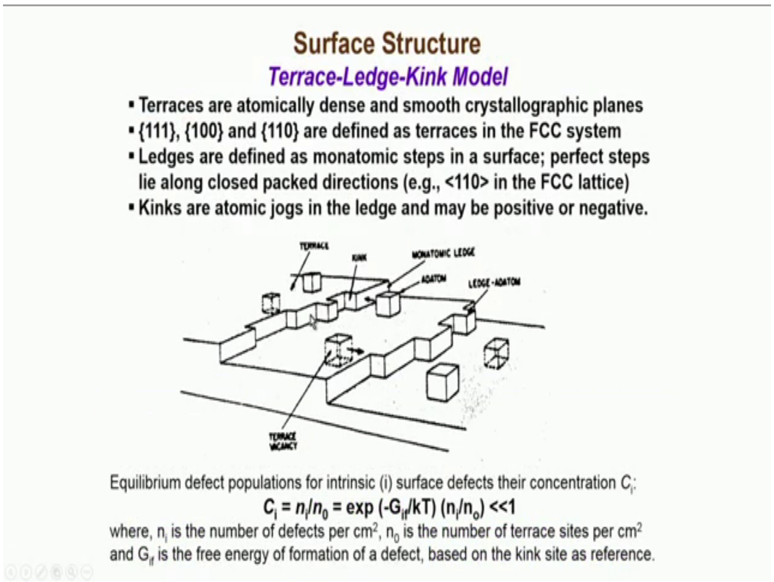

Surface Structure

Terrace-Ledge-Kink Model

- Terraces are atomically dense and smooth crystallographic planes
- {111}, {100} and {110} are defined as terraces in the FCC system
- Ledges are defined as monatomic steps in a surface; perfect steps lie along closed packed directions (e.g., <110> in the FCC lattice)
- Kinks are atomic jogs in the ledge and may be positive or negative.

Equilibrium defect populations for intrinsic (i) surface defects their concentration C_i:

$$C_i = n_i/n_0 = \exp(-G_{if}/kT)\,(n_i/n_o) << 1$$

where, n_i is the number of defects per cm^2, n_0 is the number of terrace sites per cm^2 and G_{if} is the free energy of formation of a defect, based on the kink site as reference.

Now, when the crystals grow then it actually grows in certain it develops, certain contours, certain morphology and if we divide the entire realm of solids into two major categories where, we have a for example, metallic crystals and non-metallic crystals. So, for non-metallic crystals which very well could be ionic crystals, we when the crystals grow we do see such a ledge growth mechanism in operation. In other words, since the atomic bonding energy is very high in such ionic crystals, the atoms usually will not be able to come and sit anywhere on top of the existing surface.

For example, if you imagine this is a flat terrace or a flat surface and here is a atom which comes from the vapour phase and jumps across the vapour solid interface and tries to associate itself with this solid surface, then for every such jump you have to incorporate. If you imagine this atom to be a cube then out of the 8 faces of the cube only one face which is interfacing with this existing surface is getting annihilated, but in the process you are also exposing 5 new surfaces.

So, any such jump where a single isolated atom is trying to incorporate itself with an existing solid will be energetically not favourable because you are creating more number of surface than the number of surfaces you are annihilating in the process. So, a single atom coming and getting attached or associated with a flat interface which is that for example, of an ionic crystal is unlikely.

On the other hand, if you have such kinks or if you have jogs, then such an atom can actually come and sit in this gap and when it sits in this gap, then actually you annihilate one two three interfaces on this in inner surface for any such atom to come and sit on top So, it is not only one two three also the bottom surface gets annihilated or you do not need to create a new surface for that; the only new surface that you create is the top surface. So, energetically incorporation of an atom a single atom in such a kink kinks ledge often growing interface is favourable.

Now this again requires a much longer discussion, but the point I am trying to make is that if you are dealing with metallic surface then incorporation of an atom on to the growing interface or solid liquid or solid vapour interface is much easier, and as a result a metallic crystal can take any shape. Whereas, when you are dealing with ionic crystals with very high bond energy then the surface morphology will not be random, but will maintain certain preference of orientation and geometry. And this is because the surface energies are vastly different between the metallic and ionic crystals.

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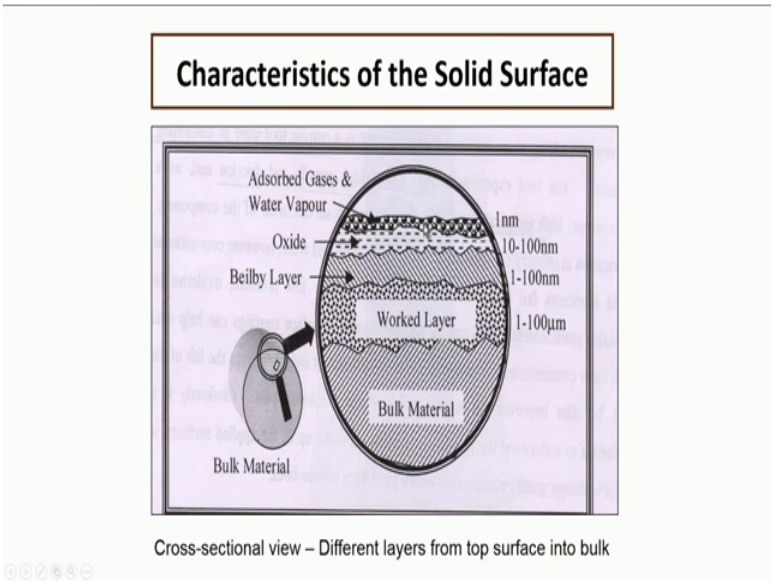

Characteristics of the Solid Surface

Cross-sectional view – Different layers from top surface into bulk

Finally, I need to tell you that if you take the cross section of any solid we tend to believe that we in a naked eye under our naked eye we see as shining flat surface. But actually, if you look at, if you zoom on and then if you zoom in and if you look at the various possibilities of atomic distribution across the on the cross sectional plane. Then on the top surface you will always see an adsorbed layer of gases or water vapour and this usually is an oxide or an hydroxide surface layer The depth or the height of it is hardly a nanometre or even less, below that will be a typically an oxide layer and this oxide layer is actually is manifested as an oxide.

So, the top layer is only an adsorbed layer which essentially just one or two atomic layers, but below that we have a solid which maintain which jump which compositionally is different from the bulk and is an oxide or an hydroxide. Below that we may actually see a highly deformed layer and in there is a large possibility that this layer could be a non-crystalline.

Even if the bulk sitting below is crystalline and such layer happens or arises because of the various kinds of mechanical processes that we subject the crystal too. For example, while preparing the crystals we subjected to very heavy amount of grinding and polishing and that can destroy the two dimensional periodicity and make such an amorphous layer, but the layer thickness again is very very small much less than 100 nanometre. So, it could be just a few nanometres, and then we have of course, a certain amount of deformed layer where we have density of various kinds of defects, but essentially below we have the solid that we generally tend to deal with.

So, in other words what I am trying to say is that when we talk of a big a bulk solid, we tend to believe that this bulk is exactly the same throughout. We just saw that the top of this solid the solid vapour interface is structurally different and certainly carries a certain amount of energy. And origin of such differences in structure and energy is better understood when you actually zoom or zoom into this kind of cross sectional plane and go layer by layer. And then you realize that first 1 or 2 nanometres, then a few tens of a nanometres and then again another tens of nanometres could be very different structurally and compositionally then what you have in the interior of the crystal.

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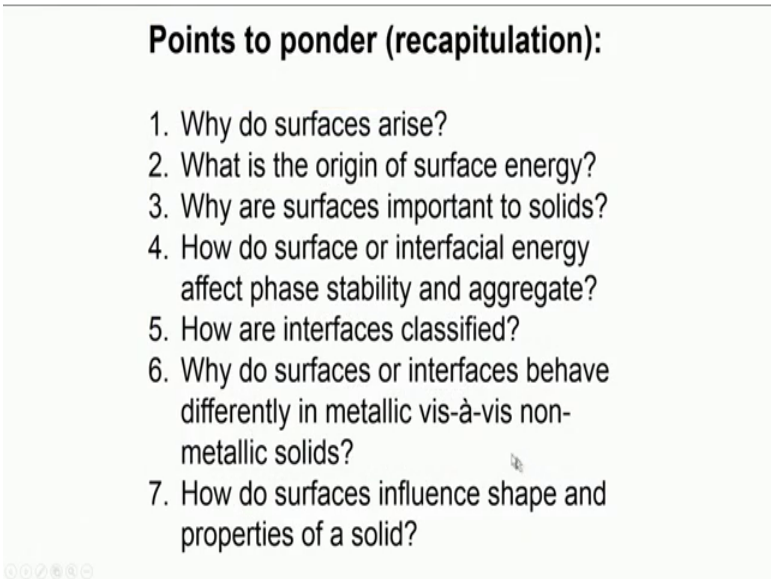

Points to ponder (recapitulation):

1. Why do surfaces arise?
2. What is the origin of surface energy?
3. Why are surfaces important to solids?
4. How do surface or interfacial energy affect phase stability and aggregate?
5. How are interfaces classified?
6. Why do surfaces or interfaces behave differently in metallic vis-à-vis non-metallic solids?
7. How do surfaces influence shape and properties of a solid?

So, now it is time to summarize; so, what did we learn. First, we have to we understood that why do surfaces arise, we have no choice whenever you talk of a solid it has a finite volume. And because of this finite volume, you certainly will have an external surface and this surface carries certain energy and hence it is this surface energy which is important for us to know.

So, we also talked about the why are these surfaces important for solids because they actually explain quite a few phenomena that is a common place for all these solids. For example, while a solids some of the solids or metals rust while some of them develop certain chemical layer on top which is different than the bulk. Why certain surfaces behave as hydrophobic, while some others could be hydrophilic the so called a hydrophobicity or the lotus effect can come either because of the structural reason or because of the compositional region reason, but is easy to explain in terms of the contact angle which in turn is related to the surface energy.

So, we classified the interfaces in various forms and we; I gave you the basis for such classification, and what is important for us is to know that the surfaces; actually differ from one another in terms of can differ from one another in terms of angle of misorientation, and the amount of energy or the degree of coherence between the neighbours and so on.

Finally, we also realized that the natural shape of a crystal is also very significantly affected by the surface energy and hence the and because the missing bonds at the surface could vary from metallic to non-metallic or ionic crystals. And as a result, we always tend to see that ionic crystals manifest themselves with flat interfaces or faceted interfaces, and metallic crystals can take any type of shape we want when we pour for example, liquid metal into a particular container and then cast a particular product.

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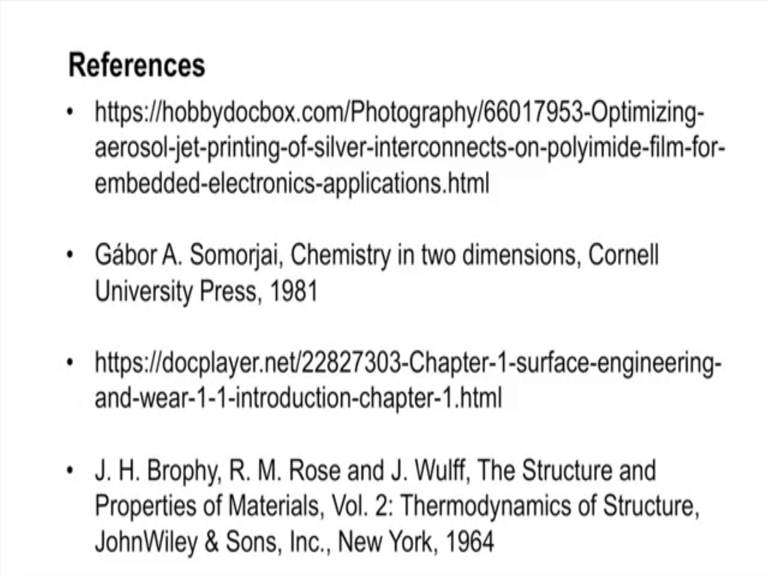

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So, with this we come to an end to this the 4th lecture of the series and now onwards we will have to move on and discuss various surface dependent properties.

Thank you very much.