Surface Engineering for Corrosion and Wear Resistance Application

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Lecture – 03
Defects in Crystalline Solids

Welcome to the 3rd lecture of this particular course on Surface Engineering. In the first lecture we talked about structure of solids and talked about both crystalline and non-crystalline solids and then we discuss about the evolution of microstructure, how it evolves in various materials processing techniques, the microstructure of solids and how it affects the properties.

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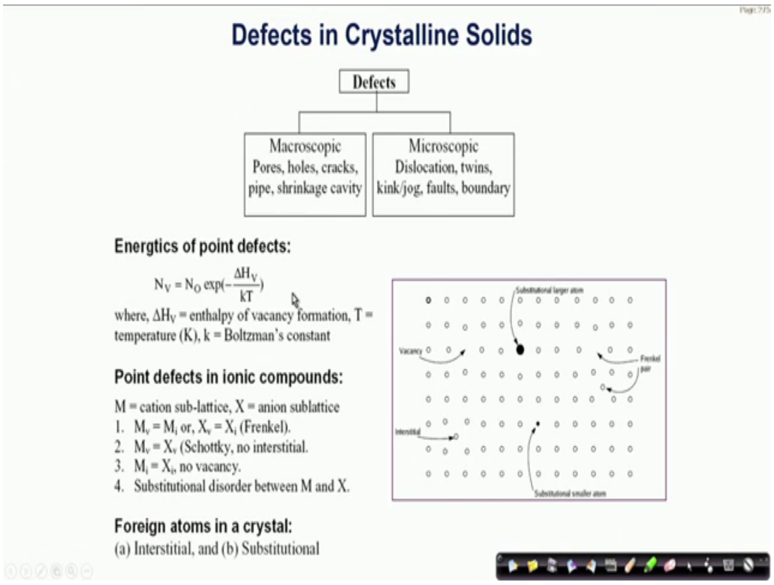

Defects in Crystalline Solids

Defects

Macroscopic
Pores, holes, cracks, pipe, shrinkage cavity

Microscopic
Dislocation, twins, kink/jog, faults, boundary

Energtics of point defects:

$$N_V = N_O \exp(-\frac{\Delta H_V}{kT})$$

where, ΔH_V = enthalpy of vacancy formation, T = temperature (K), k = Boltzman's constant

Point defects in ionic compounds:

M = cation sub-lattice, X = anion sublattice
1. $M_v = M_i$ or, $X_v = X_i$ (Frenkel).
2. $M_v = X_v$ (Schottky, no interstitial.
3. $M_i = X_i$, no vacancy.
4. Substitutional disorder between M and X.

Foreign atoms in a crystal:
(a) Interstitial, and (b) Substitutional

So, today we are going to discuss about the Defects in Crystalline Solids, it also means that defects could be present in non-crystalline solids. But for the time being let us discuss the kind of defects, we see in crystalline solids when we talked about structure of solids and particularly discussed about the crystalline solids. We discussed about the point lattices, unit cells, Bravais lattices crystal systems Bravais lattices and crystal structures, but nowhere did we mention about the possibility of presence of defects.

In fact, thermodynamically presence of certain amount of defects particularly the point defects up to a certain density actually makes the crystal more stable because of entropy contributions that we will discuss some other time. So, the point I am trying to make is that presence of defects is unavoidable in all kinds of crystalline solids. And these defects actually could be of mainly two types like you are seeing here, the macroscopic defects as the name suggests we are talking about defects, which could be seen by naked eye or at low magnification. And these could be for example, the pores or the porosities, the various kinds of shrinkage cavities leading to holes and formation of pipes in cast structures, even there could be cracks on the surface of various sizes and dimensions.

These are visible as I said under the naked eye or at low magnification maybe with a magnifying glass, but there are plenty of other defects. In fact, in these defects as I said are ubiquitous in crystalline solids and they are of different dimensions, sizes and complexities. And usually they are never present in completely pure form they are always present as defect complexes, and these are called microscopic defects because you cannot see them under the or even not even in always in optical microscope. So, you need certain resolution and magnification.

So, the first point is why we see these defects and what are they how do we classify them and how do they affect the properties and so on. So, first let me mention that we are when we are talking about defects in crystalline, solids, dimensionally the first kind of defects that one needs to discuss other point defects the point defects as the name suggests is zero-dimensional defect; so, essentially you are talking about either a missing species or an extra species coming into the lattice. For example, if any of the usual atoms or ions or molecule in a given three-dimensional periodic array is substituted by a bigger one like the one you are seeing here, then you call it a substitutional atom or maybe an substitutional ion.

You may also see this there is no necessity that the atomic radius of the substitutional atom always has to be bigger than the lattice atoms, it can be even smaller. You may also have a situation where some of these atoms could be missing during the crystal growth for kinetic reasons maybe some of the locations which are usual were missed out. An atom failed to occupy a particular position or during different types of transformations or processing, some of the atoms may find its way all the way to the surface. So, in such a situation it leaves behind a vacant spot and we call them simply vacancies.

If some of these atoms are small enough or a foreign atom which is smaller than the lattice atom and much smaller than the lattice atom then it can find its way into the lattice not occupying a usual site, but goes into a position which is non-unusual or in other words not a very regular position and we call them interstitial position. Now this is where you have to recall that I did mention that in a given lattice you certainly have certain holes present and these are unavoidable because if you try to fill up any given space or volume with hard rigid solid spheres then obviously, you cannot fill up the entire volume and some portion will be left out.

And the portions which are left out for example, here these portions actually will have a certain dimension and if you try to fit in another sphere into these kind of holes or vacant spaces, there is a limit unto which you can accommodate. And the maximum diameter that one can actually calculate in these kinds of holes will determine what would be the possible size of an interstitial atom that can fit in.

So, when you have these vacant sites for example, in a given lattice if you have a N naught number of lattice sites and a fraction of them is actually found vacant then the number of vacancies that you can find in a given lattice. Actually will be dictated by this kind of an r headiness relationship where delta H v is the enthalpy of vacancy formation, k is the Boltzmann constant and T is temperature.

So, as we can see that higher the temperature, higher willing the number of vacancies that can be present or accommodated in a given crystal. But this is about the case when we have a non polar system when the atoms are neutrals, but as I said instead of metallic systems. You may also have ionic crystals where you may have at least two kinds of species, the cations and anions and the number of cations in a given lattice could be more than one type.

But let us say in a simple case where we have an ionic crystal where M is the cation and X is the anion and so, M goes to the cationic sub lattice and X goes to the anionic sub lattice in a situation in like this you expect that M goes to the positions identified for M and X goes to the positions identified for X.

And if all of them are exactly where they are they should be then the crystal is perfect, but that is that is unlikely and nature actually dictates that if you have a certain amount of vacancies in a given lattice, then there is a position then there is a possibility of introducing randomness, and that is how you can increase the entropy. And if you consider Gibbs energy as the stability index of any given system which has two components, the enthalpy and entropy. And the entropy part essentially increases and as a result the stability of the system dictated by delta g decreases and every system in universe actually tends to go towards lowering of Gibbs energy.

So obviously, increasing randomness increasing entropy and that is how decreasing delta g goes to stabilize the system; so, having a certain amount of vacancies in a crystal is actually beneficial for the stability of the crystal. Now talking about the ionic compounds which we were just mentioning a few minutes ago, we can have a situation where certain cations actually moves to an ionic sub lattice.

So, so, if you have moves to an interstitial position; so, if you have one of the cation moving to an interstitial position. Then for example, if this particular cation moves to if a particular cation moves to an interstitial position and it balances with a vacancy in a in another position then the charge neutrality is maintained and yet you can have a defect created in the crystal.

So, this is kind of a defect is called Frenkel defect and where we actually have the identical number of vacancies in cationic sub lattice compensated by number of interstitial in the cationic sub lattice. A similar thing can also happen for the anionic sub lattice, and that is how you can maintain the charge neutrality. You can also have vacancies both in both in cationic sub lattice and anionic sub lattice.

So, in case of Frenkel disorder we actually have equal number of vacancies and interstitials either in the cationic sub lattice or in the anionic sub lattice. In case of schottky disorder we have equal number of vacancies and interstitials in equal number of vacancies in cationic and anionic sub lattice. You may also have disorder coming purely because of the substitution between the either in the cationic or the anionic sub lattices. So, essentially a foreign atom can go either into the interstitial position or the substitutional position.

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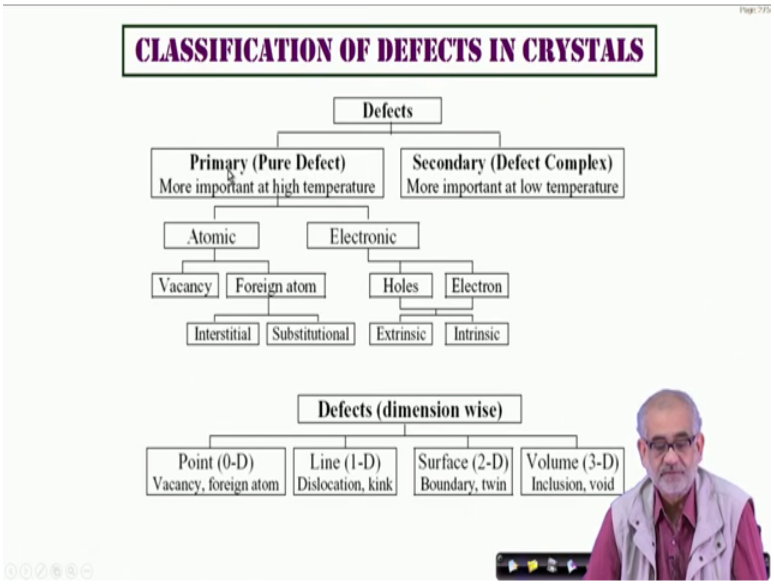

CLASSIFICATION OF DEFECTS IN CRYSTALS

Defects

Primary (Pure Defect)
More important at high temperature

Secondary (Defect Complex)
More important at low temperature

Atomic

Electronic

Vacancy

Foreign atom

Holes

Electron

Interstitial

Substitutional

Extrinsic

Intrinsic

Defects (dimension wise)

Point (0-D)
Vacancy, foreign atom

Line (1-D)
Dislocation, kink

Surface (2-D)
Boundary, twin

Volume (3-D)
Inclusion, void

Now, overall landscape of the possible defects allows you to classify them into, so called primary and secondary kind of defects where primary essentially means pure defects which are usually present only at a high temperature. So, you where you have you can have defects in the with regards to the atom or defects related to the electrons so, you call them atomic disorder or electronic disorder.

And in case of atomic disorder we just heard we just discussed that we can have vacancies or we can have foreign atoms, in the foreign atoms could either be interstitial or substitutional. And electronic defects could actually create either a hole where an electron is missing at a particular situation in a crystal which has a certain band gap or we can have excess of electrons.

So, either holes or electrons they could be either extrinsic or intrinsic depending upon the compositional variation of the system. By way of increasing the temperature you can create differences in the density of electrons or holes or by changing the composition you can create a similar defect density.

Now all these entire range of defects that we talked about these are called primary defects because they are isolated and independent, but very rarely in a crystal you see a situation where you have isolated pure defects. So, for example, usually a vacancy will have some relation with an interstitial or a substitutional atom. Similarly holes and electrons can make pairs; so, this kind of pairs actually make them gives rise to what is known as defect complexes and they are called the secondary defects. And as it is written here these kind of defects are more prevalent at low temperature or usually in the working condition.

But in a crystal, which actually is not having any electrical character or in other words typically a metallic crystal one can define the various types of defects, typically in terms of dimension and that the four types of defects that we can talk about would be the point defects which is zero-dimension these is this is basically the terminologies which is used as per convention.

So, all point defects are considered as zero-dimensional defects, line defects are called like dislocations and kinks are called one-dimensional defects, surface defects are two-dimensional defects and similarly or finally, you can also have volume defects which are typical examples would be inclusions voids and so on.

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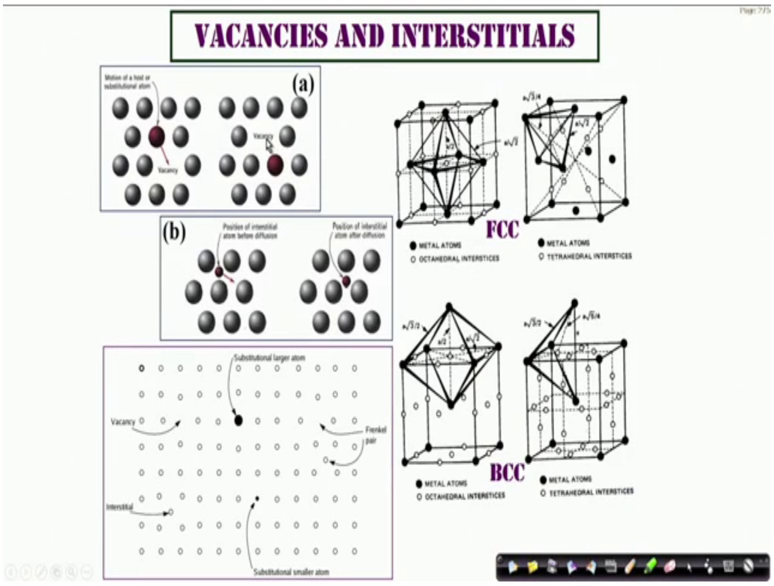

VACANCIES AND INTERSTITIALS

Now, this is how you actually can create a vacancy. So, for example, if you have an; so, how do they actually help or how do they affect the properties. So, for various processes either for transformation or for mechanical deformations or various kinds of shape changes we need atomic mobility. And an atom always finds it easier to jump into a next possible site a neighboring site, if that site happens to be vacant.

So, this fellow actually can easily go to the next neighboring vacancy vacant position because this is the easiest way to move and when this atom moves to the vacant site then the vacancy always exchange its position and goes back into there so. Once this atom moves to the vacant site then we create a situation like this where we have a vacancy where we have an substitutional atom.

Now, moving into the earlier vacant site and the vacancy in turn has moved back into the earlier into a substitutional site. And this kind of a process can move or can continue so long the atoms have sufficient amplitude of vibration or in other words temperature is high enough for such jumps to take place.

We can also have a situation where interstitial atoms are present and for an interstitial atom to move you do not have to create a vacancy. So, the probability of jump of an interstitial atom to its next position is always higher and hence the activation barrier for diffusion or solute transport for interstitial atom would always be lower and easier than compared to the situation where you are dealing with substitutional atoms.

Now, all these so called interstitial positions that we are that we need for interstitial diffusion or interstitial vacant sites creation and so on; we just we did see this view diagram before and let us recall that I did mention that in an FCC crystal, you expect the atoms to be at the face centering positions and the corner of the atoms. So, essentially 8 corners and 6 face centering positions are occupied. So, one-eighth into 8 plus one-sixth into 6 half into 6 will make it 3 plus 1 plus 3. So, you essentially expect in an elemental FCC crystal 4 effective number of atoms per unit cell.

But when you say that you expect atoms to occupy it corners and fascinating positions then the centers of the edges and the center of the cube or center of the unit cell obviously, are lying vacant and the diameter of such vacant hole is the largest. So, this is how you can actually define a possible interstitial vacant site and it and its size in an FCC crystal, but since this vacancy here is surrounded by 1 2 3 4 5 and 6 atoms. So, you have essentially you can imagine as if this central position is surrounded by 8 faces or surfaces of triangular shape and hence you call this an octahedral void.

So, an octahedral void will be coordinated by 6 atoms and 8 surfaces similarly, in an FCC crystal one can see a tetrahedral void which essentially is located as at the equivalent of one-fourth, one-fourth, one-fourth position and is surrounded by 4 nearest neighbors and 4 planes. So, this is called the tetrahedral void or tetrahedral interstitial site and since this is geometric where we can actually calculate exactly the length of these arms we also should be able to calculate exactly what is the diameter of these vacant sites.

So, this kind of interstitial position their size, their location can be geometrically determined using such considerations both for FCC BCC and for that matter any other kind of Bravais lattices.

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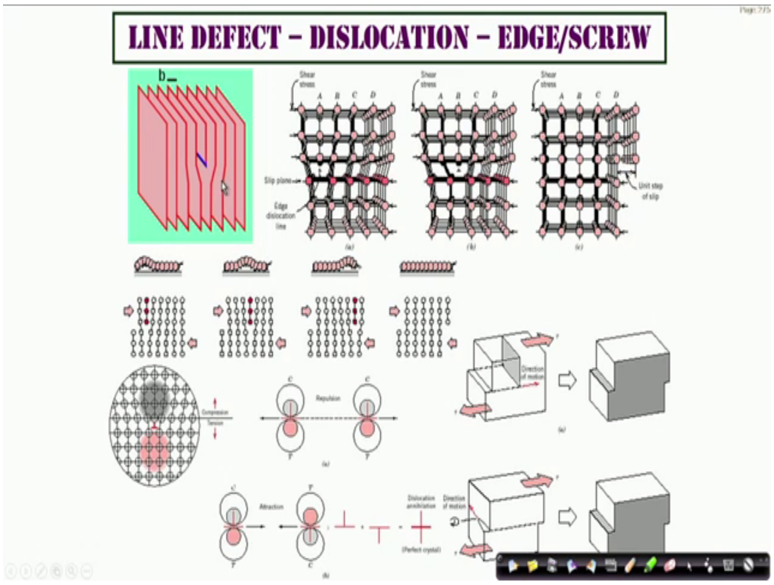

LINE DEFECT – DISLOCATION – EDGE/SCREW

So, so far we talked only about the point defects; now, what if you imagine a situation that we have these kind of planes which are equidistant because they are part of a crystal where we have long range periodicity. And for whatever reason if we also happen to discover an extra half plane introduced in between sort of squeezed in between, then if you create a burgess circuit or so called if you define a circuit around this kind of a situation where you have both a defect and a non-defective lattice let us say you start from here.

So, if you go one if you go 1 2 3, then come 1 2 3, then again go 1 2 3 then you realize that you actually are going out of the crystal. So; that means, there is a closure failure and the closure failure dimension wise and direction wise defines a particular character characteristic feature called burgess vector which defines exactly the existence and the dimension of a so called edge dislocation. So, you can have whenever you have such an extra half plane introduced inside the crystal, this blue line here defines the end of this extra half plane.

So, if you now imagine a plane which is perpendicular to this set of planes, then on that particular plane or face the intersection of this extra half plane and the plane which is now called the reference plane and perpendicular, the intersection will be aligned because intersection between two surfaces always will be aligned. And this intersection line is the so called dislocation line and this is why we call it a line defect and these line defects by definition or convention can either be edge dislocation which is what we have discussed now. You can also have a situation where use because of certain twisting of the crystal, you actually can see creation of another kind of a dislocation which is called screw dislocation.

So, if you imagine a helical path around a particular line so, and which happens because of the twisting of this crystal or shearing of this crystal along this particular axis of rotation, then this would this is how you actually can create screw dislocation. So, no matter essentially we have a situation where we have either line defects or line defects either edge or screw, we make and these dislocations either edge or screw is very very important because they account for the deformation or shape change of all crystalline solids particularly in the metallic crystals.

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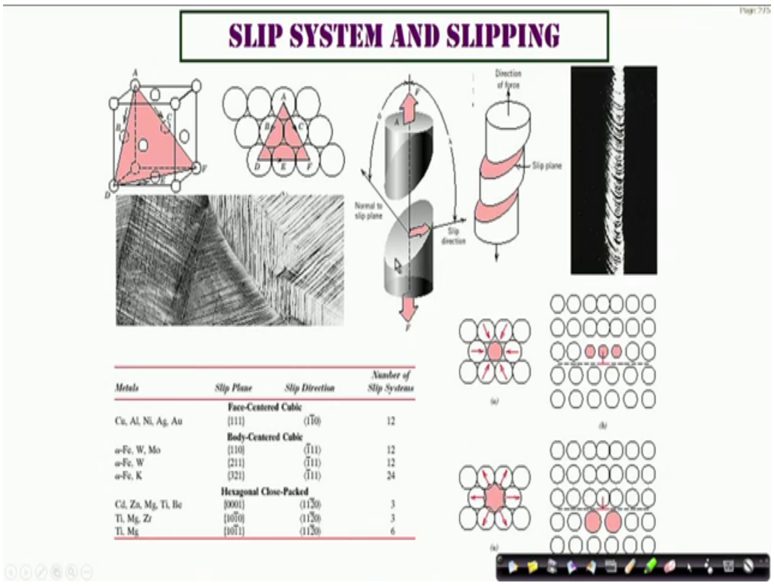

SLIP SYSTEM AND SLIPPING

Metals	*Slip Plane*	*Slip Direction*	*Number of Slip Systems*
	Face-Centered Cubic		
Cu, Al, Ni, Ag, Au	{111}	⟨1$\bar{1}$0⟩	12
	Body-Centered Cubic		
α-Fe, W, Mo	{110}	⟨$\bar{1}$11⟩	12
α-Fe, W	{211}	⟨$\bar{1}$11⟩	12
α-Fe, K	{321}	⟨$\bar{1}$11⟩	24
	Hexagonal Close-Packed		
Cd, Zn, Mg, Ti, Be	{0001}	⟨11$\bar{2}$0⟩	3
Ti, Mg, Zr	{10$\bar{1}$0}	⟨11$\bar{2}$0⟩	3
Ti, Mg	{10$\bar{1}$1}	⟨11$\bar{2}$0⟩	6

As because deformation using such line defect is energetically always more favorable because it requires less an amount of shear stress compared to a situation where the crystal is all perfect. So, the defects have a role to play for not only defining the stability, but also defining certain characteristics or deformation behavior or in general bulk or surface properties of the crystal.

This actually requires a much longer discussion so, which is not really within the purview of this particular course, but we are since we are talking about structure of solids. We need to at least make a reference to the fact that when we talk of crystals, we certainly will also have to remember that there could be defects which are dimensionally which could be dimensionally 0 1 2 and 3 dimensional defects.

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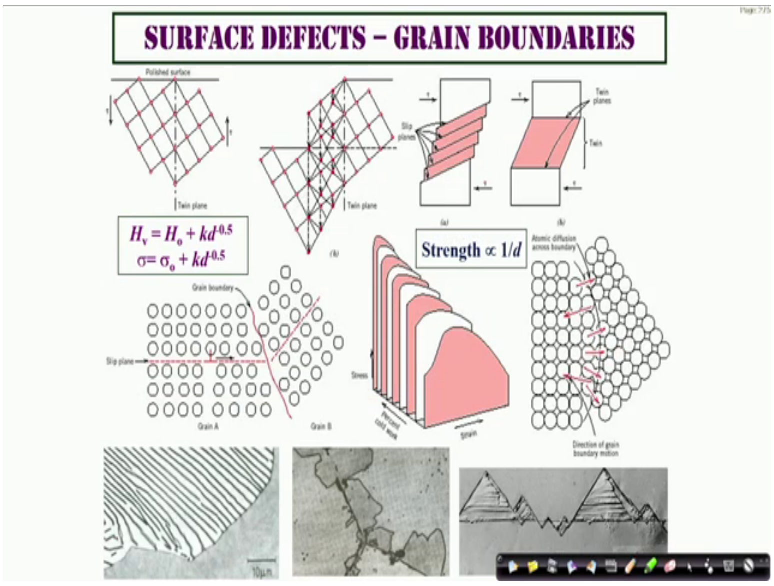

SURFACE DEFECTS – GRAIN BOUNDARIES

$H_v = H_o + kd^{-0.5}$

$\sigma = \sigma_o + kd^{-0.5}$

Strength ∝ 1/d

So, we have talked about zero-dimensional, we have talked about one-dimensional and now we need to talk about two-dimensional defects. And these two-dimensional defects are actually they arise because we when we talk of crystals or for that matter if you simply join two solids irrespective of whether they are crystalline or non-crystalline.

So, if you just take two solids, and if you join the two solids at the interface or the boundary you certainly will see certain disruption of continuity. And because of such a disruptions for example, if you consider this to be one of the one part of the crystal and this is another part of the crystal. You clearly see that the orientation here is different than the orientation on the crystal on the crystallite on the right.

So, this is a line which will delineate the differences in such orientation and hence this will be called a boundary. If the two phases across they are same or similar then you will call them simply the grain boundary by similar what I mean is that they are actually of the same crystal structure and hence I say and also the same composition. But you may also have a situation where the crystallites on either side need not be having the same crystal structure or the same composition and in that case you create another kind of a boundary known as phase boundary.

So, the point is if I have such boundaries present then for a dislocation which we just heard as the main agency required for explaining or defining any kind of deformation of crystals. Such a dislocation can find its way all the way up to the boundary, but then will face a barrier across the boundary because the continuity changes here or in other words the orientation changes. So, the stress which was responsible for the dislocation to move it all the way up to the boundary will no longer be able to move this particular dislocation into the other domain. So, this is now a boundary between as if two countries and you have a border here so; obviously, this fellow cannot move to the next country without disrupting.

So, when it stops; that means, that deformation stops and the strength increases. So, if you have if you introduce number of such boundaries then the strength gradually will increase because such barriers to dislocation movements increase. This is a simple explanation as to why strength of a crystal is known to increase or for that matter it could be the yield strength, it could be just simply hardness. So, either way this mechanical strength increases as the size of the crystallite also called a grain size decreases, and this is this famous hall page relationship which many of you probably already know which simply say is that smaller grain size greater the strength of the material and that strengthening arises purely because of the barrier posed by these boundaries to dislocation movement.

So, the boundaries can be as I said or either grain boundaries or face boundaries, and here are certain examples so, these are so called lamellar structures. So, each lamely is having interface with the matrix and similarly this is another interface boundary and because the phase ahead is of a different crystal structure. The boundaries can take very typical shapes where it could be sort of non-faceted or curved or it can take a shape which is very geometric and flat, and such flat and geometric boundaries arise for one set of crystals under one set of conditions whereas, such curved boundaries can also appear.

In other kind of crystals and the reason why the shapes are different is principally attributed to the surface energy individual energy associated with them which is in turn related to the crystals and crystal structure that we are dealing with, but all these various shapes are the very presence and identity of various kinds of two-dimensional defects have a have a very great experience influence on the overall properties of the material.

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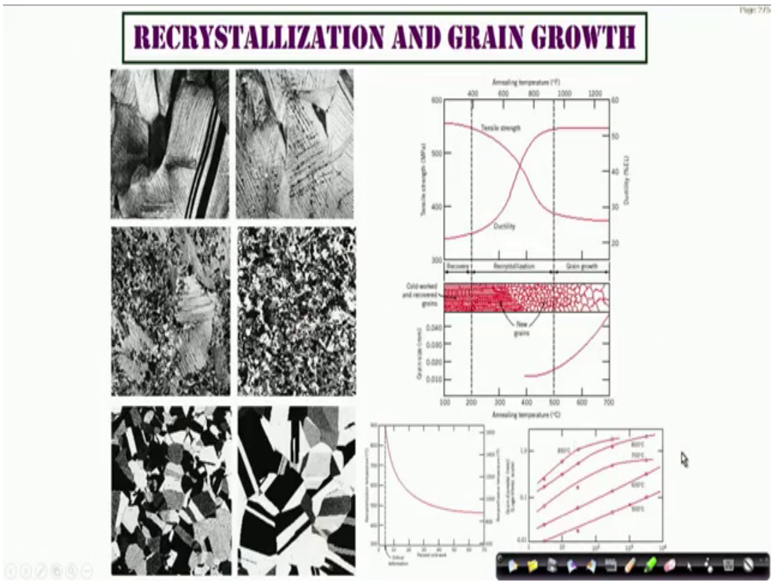

RECRYSTALLIZATION AND GRAIN GROWTH

And this is just an example to show you that how different kinds of boundaries can arise so, if you deform a material and then allow it to re-crystallize or anneal them. So, that they re-crystallize then you form very tiny little boundaries and this is how you can increase. So, the microstructure can be varied to a large extent like this if you apply different kinds of thermo mechanical processing.

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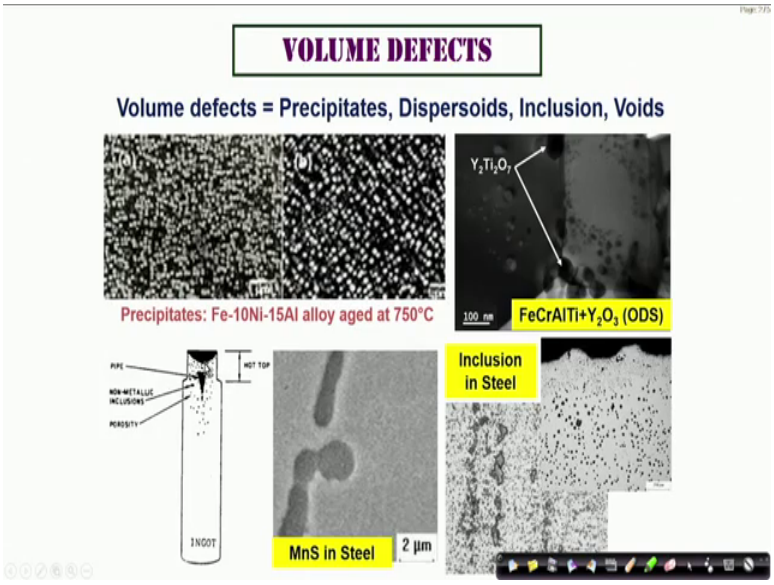

VOLUME DEFECTS

Volume defects = Precipitates, Dispersoids, Inclusion, Voids

Precipitates: Fe-10Ni-15Al alloy aged at 750°C

FeCrAlTi+Y_2O_3 (ODS)

Inclusion in Steel

MnS in Steel

Finally, we also need to touch upon the void volume defects. So, essentially dimensionally we are now talking about situations where you can have large defects so, these are macro defects, if this is an ingot, a cast ingot then we can have such pipes, we can have the shrinkage cavity, we can have various porosities, they can be small or in complexes, they can actually join together and make a larger hole and some of these could actually be easily seen by naked eyes.

But on the other hand you can have inclusions for example, manganese sulphide in steel; so, these inclusions actually are entities which have X Y Z dimension so, they are three dimensional. So, these are inclusions and hence these are undesirable, but in specific situations we actually may desire to have certain three-dimensional defects in a crystal like precipitates or externally added dispersoids. And these kind of entities three-dimensional entities can vastly affect the mechanical properties of a material. And so, in some cases they are undesirable in some other cases they are desirable, but the fact remains that dimension wise they are different.

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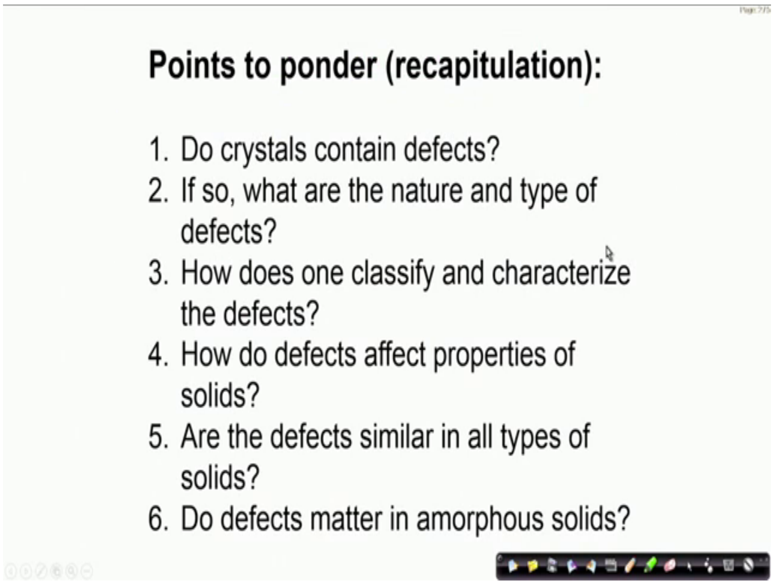

Points to ponder (recapitulation):

1. Do crystals contain defects?
2. If so, what are the nature and type of defects?
3. How does one classify and characterize the defects?
4. How do defects affect properties of solids?
5. Are the defects similar in all types of solids?
6. Do defects matter in amorphous solids?

So, we would now like to wind up or summarize as to what we discussed now. First of all we do realize that crystals when we describe them from ideal point of view tend to gives us an impression as if they are all defect free, but in reality all real crystals will carry defects. And one of the reason I attributed already that having certain density of point defects actually increases the stability of the crystal. So, every system in universe tends to get minimize its Gibbs energy and one way of reducing that for crystalline solids is when you actually reduce, when you have certain density of defects.

You also have for example, the defects which are of different types and of different nature and we discussed those various types of defects among the point effects, among line defects and various other defects. So, we can classify the defects in terms of dimension, in terms of their origin and we also discuss how we can characterize these defects. What is even more important is that how do these defects affect the properties of solids, and this properties by that I mean both structural as well as functional properties. For example, having point defects can make a lot of difference in terms of conductivity or band gap of a crystal having line defects can make a lot of difference in terms of ductility or strength of a material.

Defects are present in all kinds of solids not only crystalline solids, but today we discussed only about the possibilities of defects in crystalline solids. But we do have certain defects for example, the same point defects or cluster of vacancies or what is known as shear bands in amorphous solids and they actually matter a lot in terms of explaining various kinds of functional and structural properties in solids.

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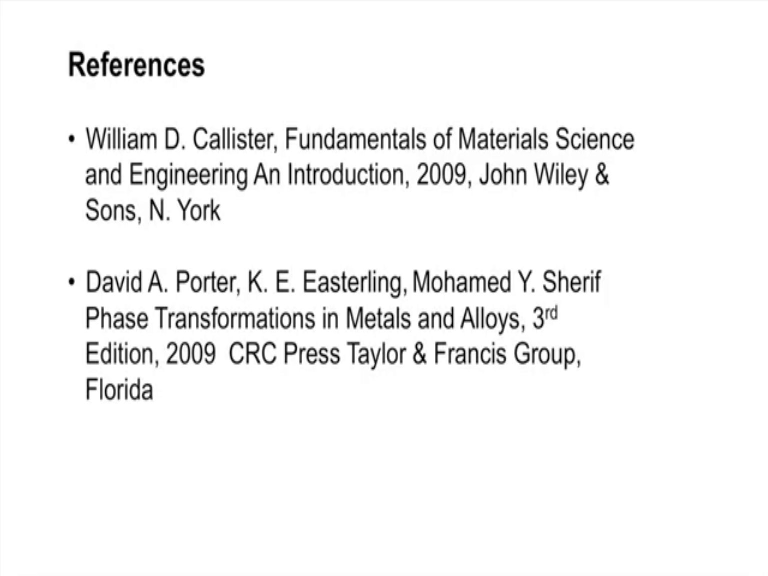

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So, with this we conclude now, and in the next lecture we will discuss the various kinds of; we will discuss the origin of surface energy and the various other effects that surfaces have on the properties of crystal.

Thank you very much.