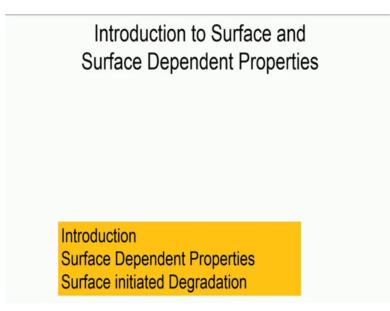
## Surface Engineering for Corrosion and Wear Resistance Application Prof. Jyotsna Dutta Majumdar Department of Metallurgical and Material Engineering Indian Institute of Technology Kharagpur

Lecture – 07 Surface Dependent Properties and Surface initiated Degradation

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Hello, welcome to lecture number 7 of this series. So, in this lecture I will discuss about the, surface and different surface dependent engineering properties.

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Surface
Surface may be defined as the interface between two phases or two grains in the same phase.
Why is surface Important
Why is surface Important It's the region of a highest energy

So, surface phase a very important role in determining many important properties of metal and it is nothing but, may be defined as the interface between two phases or two grains in the same phase. Surface is very important because, it is the region of highest energy, it faces the environment and this is the part of the component where, stresses are often highest. And, as a result of which you will find that, on the surface there are very important phenomena and also many important degradations also they initiate from the surface.

So, unless and until, we understand the surface, it is very important to design the surface of any component for having that tailor man in it is properties.

 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 per m<sup>2</sup> of surface).

 Surface energy

 Surface energy

 Surface energy

 Surface energy

 Surface energy

 Surface energy

 Excess energy per unit area associated with a surface. Unit of surface energy is ergs/cm<sup>2</sup>.

 Magaitude of Surface Energy

 Surface Energy

 Schematic Diagram of Coordination Change of Atom at Solid-Aquid, figuid-gas and gas-solid Interface

 J. H. Brophy, R. M. Rose and J. Wulff, The Structure and Properties of Materials, Vol. 2: Thermodynamics of Structure, JohnWiley & Sons, Inc., New York, 1964

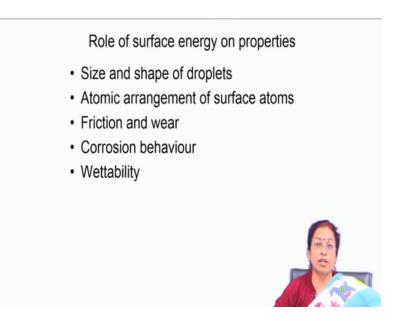
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So, if you talk about the surface then first thing which, comes into mind is nothing but, surface energy. Surface energy is nothing but, the extra energy which is required to create the surface. So, it is actually represented in terms of specific surface energy, this is the excess energy per unit surface area. So, the unit is joules per meter square of surface. Now, it is basically nothing but, it depends on the interface actually. So, you can understand that surface may be that what are the surface energy or interfacial energy, it is very much dependent on the environment.

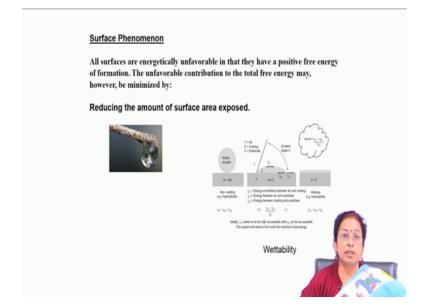
Whenever you talk about the surface area interfacial energy between solid and liquid, it is having some energy value on the other hand, if you talk about the interfacial energy between solid and gaseous species, it is having some energy value on the other hand, when you talk about the different planes on the surface, it is having different energy values. So, it is required it is very much dependent on the environment and also many other parameters on the surface particularly, at which plane the surface is created and it is nothing but, because of the fact that when you create the surface, we need to break certain amount of certain number of bonds from the surface to create the interface and as a result of which surface energies, we need to spend some energy to create the surface.

So, for example, this is the case for the solid to liquid interface, if it is FCC metals then naturally, it is having the and if you create the surface alone 1 1 1 plane then, it is having the coordination number of 9 and you should like to create the that solid gas interface then, naturally you have to break 3 numbers of bonds to create the surface between the solid and gaseous species. So, we could depending on the number of bonds which you are breaking, the surface energy also varies.

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Now, if you talk about the role of surface energy or each the implications are important. So, you find that, it influences many important phenomena like for example, if you talk about size and shape of the droplets then, atomic arrangement of the surface atoms then, friction and wear behaviour, corrosion behaviour, wettability. These all phenomena they are dependent on the surface energy and the driving force is nothing but, the free energy change associated with lowering of surface energy. So, whenever surface is having you create the surface there is a increase in energy naturally, the driving force is nothing but, lowering of it is energy.



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So, if you talk about different phenomena, that occurs on the surface or that are influenced by the surface energy, these are like droplet dimension, when you go on having a kind of molten metal and if you just go on pouring it you will find that it will be poured in a droplet life fashion. Or, otherwise when you prepare the synthesized powder, you will find that by water atomization or maybe gas atomization technique, you will find that it is shape is always vehicle initial because, when it is vehicle initial and say it is having very low surface energy because, of it is very high surface area.

So, naturally that one of the important phenomena is that, related to surface energy is droplet size and another phenomena which is very important and it is nothing but, the properties of the material that is wettability which is again driven by the surface energy. So, you will find that depending on the surface energy, your wetting behaviour will vary. So, wettability is measured in terms of the contact angle. So, you will find that for example, when the liquid is poured on the surface of the solid, it may spread or otherwise, it may retain the dimension of sphere.

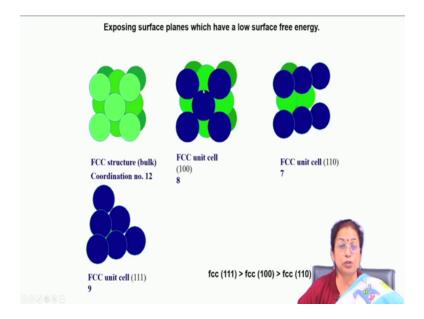
So, when contact angle is quite high you call it as a hydrophobic surface when, it is a low it is called you call it as that hydrophilic surface and whole things are driven by that the surface energy or interfacial energy. For example, when a liquid drop or a liquid droplet on the surface of the solid, there are 3 important interfaces which are created one is liquid to gas interface, one is liquid to solid interface and other one is solid to gas interface.

So, if you find that solid to gas interface and solid to liquid interface is higher than that of, it is lower than that of, solid gas to solid interface you will find that, it is hydrophobic in nature. On the other hand, if it is between minus 1 to 1, it is normal it is having normal behaviour, on the other hand when the interfacial energy between that whether that surface energy between solid to gas minus surface energy between, solid to liquid is low higher than that of that of the solid to gas you will find that, it is having liquid to gas you will find that it is behaving in a hydrophilic fashion.

So, whatever it behaves in a hydrophilic in a hydrophilic fashion you call it as it is highly wettable. So, wettable surface is having certain advantages, especially when you talk about the materials for implant by implant application, it should be highly wettable when, you talk about that self-cleaning surface, it has to be wettable on the other hand when, you talk about that high corrosion resistance coating or that particular material which has to be applied in water environment, very highly resistance to the corrosion resistance or erosion resistance, it should be hydrophilic hydrophobic in nature.

So, each and every phenomena, they are driven by it is driven by the surface energy. So, you can design their surface based on your requirement only and when and only when you know the surface energy value properly.

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Now, there is another important thing which is which controls the surface energy. So, first important factor which control the surface energy, is the area of the surface which is exposed actually, second important factor which basically controls the surface energy is the environment, third important factor which controls the surface energy is nothing but, the phase along which the surface is created or the surface plain actually. So, if you say that case for typical FCC metals, you will find that it is having the bulk coordination number of 12.

So, when you go on creating the surface, you will find that surface energy will depend on at which plane, the surface is created. If you create the surface along 1 0 0 plane, you will find that the coordination number along 1 0 0 plane is 8. So, if you would like to create the surface you need to break, 4 numbers of bond, if you would like to create surface along 1 1 0 phase or along 1 1 1 1 1 0 plane, your coordination number of each atom at this plane is 7. So, you need to break 5 numbers of bonds.

On the other hand, if you would like to create the surface along  $1 \ 1 \ 1$  plane, where coordination number is 9, you have to break 3 numbers of bonds. So, you will find that the minimum energy required for creation of surface is along  $1 \ 1 \ 1$  plane. So, if you just categorize the surface energy in ascending order you will find that, FCC  $1 \ 1 \ 1$  plane is having the typical lowest energy than that of FCC  $1 \ 1 \ 0$  or than that of FCC  $1 \ 0 \ 0 \ 1 \ 1 \ 0$ .

So, you can say that this particular plane is actually most favorable in terms of the minimum free energy.

Altering the local surface atomic geometry to reduce the surface free energy.	
Relaxed Surface (d <sub>1.2</sub> < d <sub>bab</sub> ) Reconstructed fcc(110)	
By Adsorption from Gas Phase	

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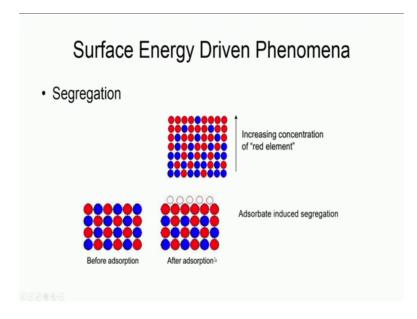
So, you can understand that depending on the plane along which surface is created, the surface energy will vary. So, another phenomena which is usually observed in metric materials or maybe semiconductor materials, when you see the surface under ultra high vacuum, that is the thing in atomic an arrangement of the surface. So, there are two important change which is which are occurred especially, when you just take the pure materials may be metallic or nonmetallic and if you see it under ultra high vacuum, you will find that your atomic arrangement on the surface or surface paints is different from that of bark of the materials.

So, the atomic arrangement is very much dependent on the forces acting on it by the other atoms surrounding that particular atom. So, when you talk about the surface atom naturally, you are breaking some of the atoms naturally, some things are basically missing on the surface. So, if you see the surface are to make arrangement you will find that, the d spacing of the surface atom and the neighboring atom is a little lower than that of d spacing of the typical inter atomic spacing of the other atoms which are in the bulk.

So, this is called relaxation and another phenomena, which is also observed that is rearrangement of the surface called reconstruction. So, reconstruction is a phenomena where you will find that, there are a missing numbers of atoms from the surface and lattice parameter on the surface is usually higher than that of lattice parameter of the same in the bulk. So, reconstruction and relaxation these are the 2 important phenomena, which are observed on the surface, when you see it under ultra-high vacuum but, on the other hand if you keep it in normal environment you will find that, the there is again the phenomena of absorption from the gas phase, which again lowers the surface energy significantly.

So, when absorption is there naturally, once it is adsorbed these all molecules, in the environment they are absorbed, you will not really get any kind of relaxation or deconstruction phenomena because, these are the phenomena which are usually observed on the pure metals and which is under ultra high vacuum, where there is no other impurities in the environment and if there are impurities in the environment, you will find that impurities they get adsorbed over the surface and depending on the kind of absorption is there, there are different names like species of strain or kimmies of strain phenomena. So, whatever may be both the cases species of strain for example, is reversible and kimmies of strain is irreversible phenomena but, in both cases you will find that, there is lowering of the surface energy to a large exchange.

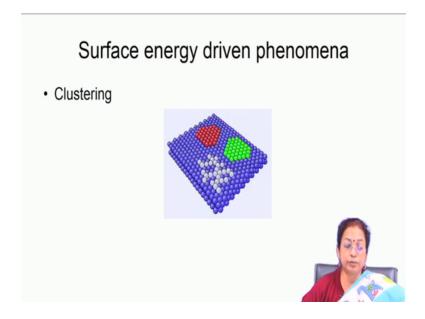
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So, apart from that there are few other phenomena which are also observed because, of higher energy of the surface one is segregation phenomena, in alloy system particularly if you see the surface concentration atomic, surface impurity concentration as compared to

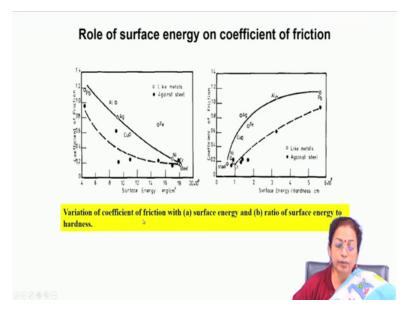
that of bulk you will find that, the most of the impured atoms or solute atoms are segregated along the surfaces, as is there in the grain boundaries.

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So, again the driving force is nothing but, lowering of the free energy, you will find lot of clustering phenomena all throughout the surface where, like atoms try to get segregated along the surfaces to minimize it is energy.

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So, now surface energy. So, these all phenomena are observed and naturally these all things change their structure of the surface as well as composition to a large extent. So, if

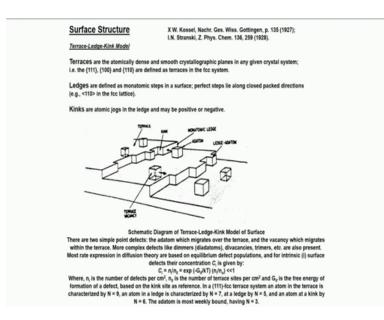
you just think of the bulk metallic materials application, whatever things happen on the surface, that might not have significant role but, naturally if you think of applications of smaller structure particularly for the MEMS devices, you will find that these things in atomic arrangement or this changing composition might have significant role, on the functional properties of the matter.

If you talk about structural properties like coefficient of friction, corrosion registrars, these are also influenced to a large extent by surface energy for example, if you see the variation of coefficient of friction it is surface energy, you will find that higher is the surface energy, you know the lowering is the coefficient of friction. Because, higher is the surface energy more will be the tendency to reduce it is energy when, another surface is there on it is on it is surface, as a result of which you will find that, lesser will be the hindrance towards the motion.

So, this is the reason behind the lowering of coefficient of friction, with increased surface energy. On the other hand, if you have if you think of the mechanical properties of the material, which has also influenced on coefficient of friction like, hardness value. There you will find that higher is the hardness naturally, higher will be the lower will be the coefficient of friction because, hardness increase whenever there is increased hardness or maybe the harder the materials are in combinations are higher harder the metal surface is naturally lower will be reduced to be the coefficient of friction.

So, naturally the relationship is very much complex in nature, you cannot say that only surface energy or only mechanical properties, which play role in determining the coefficient of friction but, a kind of combined relationship is there which create role in determining the coefficient of friction.

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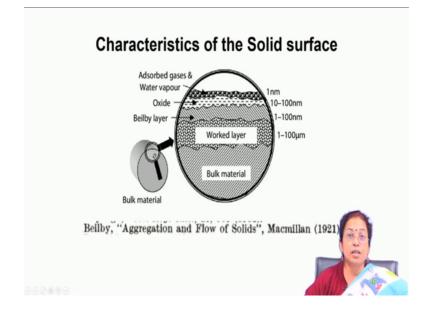
Now, if you talk about another phenomena, which is observed on the surface that is atomic arrangement of the surface. So, you will find that atomic arrangement of the surface is a little different from that of the bulk, as I mentioned you that depending on the availability of energy, the plane along which surface will be created will depend on. So, usually it is atomically dense pain along with surface is created because, it requires minimum energy to create the surface. Now, if you see the surface atomic arrangement again, this is not ideally smooth in nature, there is always discontinuities, in the atomic arrangement of the surface.

So, usually if you see the surface atomic arrangement you will find that, there are actually smooth crystallographic planes in a system up to a certain level and then there is discontinuity then, again this particular surface continues or to a certain distance and then again there is discontinuities on atomic state discontinuities.

So, this particularly atomically smooth plains where surface is created is called terrace and where there is discontinuity by one atomic level, you call it as ledges and again in the ledge you will find that this is again not continuous in nature, there is actually some of the atoms which are coming out, we call it add atoms and some space of vacancies are also created over there, some of the atomic arrangement which are deep inside you call it kinks. So, kinks ledges these are all there along that particular crystallographic plane of the ledge. So, these all phenomena you will observe, in the surface if you see under ultra high vacuum. So, this is typical terrace ledge kink model, which has been established by 3 scientists and you will find that in the surface if you see the atomic arrangement, they are really very much free to move, not only the surface energies are higher. But, also you will find that on the surface there are many free atoms, many free vacancies and creation of vacancies also need much lower energy, than the creation of vacancies inside the bulk of the materials.

So, you will find that, it is very easy to create the vacancies and as a result of which, if you talk about the phenomena of diffusion you will find that, diffusivity is along the surface is the much higher than that of but, that gain boundaries and that of bulk of the materials. Because, it is easy to migrate the atoms on the surface because, it is easy to generate defects on the surface, particularly point defects where atoms can get atom can see it and then get defused in.

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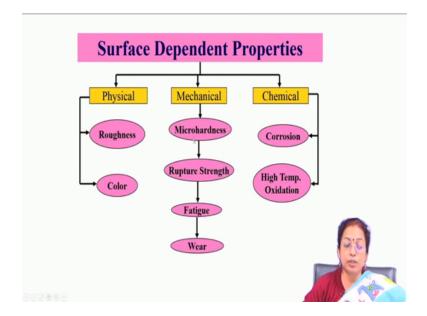


So, this particular surface arrangement is very important to know and you will find it if you see it an in ultra high vacuum and when surface is highly pure in nature. Now, if you go to a little lower scale rather, if you just go on magnifying further, if you dissolve it a little bit to a larger extent, like if you see the microscopic arrangement of the surface. But, not really atomic arrangement of the surface, you will find that depending on the zone where you are observing, the structure again varies it is nothing but, a multi-layered structure, where near the surface there are a lot of absorbed ashes and water vapor or you will find the reconstruction or maybe that relaxation phenomena, if you see it under ultra high vacuum but, if you see normal environment you will find lot of observed basis species are there, if you talk about metallic materials which are highly reactive in nature, naturally there is there is a phenomena of chemical absorption. So, kimmies of strain phenomena so, near to the surface there is always some oxide or compound layer formation and below that compound layer again, you will find very thin among first layer, which does not have any structure actually. So, it is called Beilby layer because, these particular structural features the exactly is finished is vanished on the surface.

Because, of the reason that some cold working operation, which are is the surface has undergone, prior to it is the processing actually. So, this Beilby layer is very important and it is a amorphous in nature and the presence of this layer will be visible, if you do ozo electron, X-ray photoelectron spectroscopy or ozo electron spectroscopic analysis or maybe low energy electron diffraction analysis, you will get to know about that amorphousness of this particular feature actually. If you also do the micro nano hardness analysis, you will find that, it is having little bit higher hardness than, rest of the material. Below that there is rock layer, where you will find lot of dislocations and dislocation in integument and then you will find also the elongation of the grains, which is worked layer and below that there is bulk of the material.

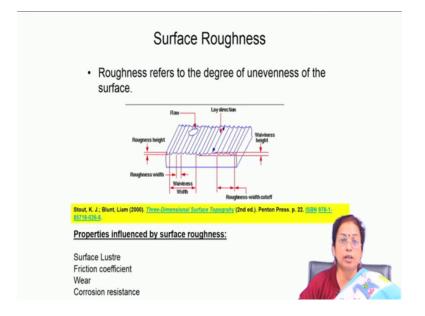
So, these all layers are very much important and if you just see the microstructure of the cross section carefully, you will find that at different scale these different layers will be visible for example, the layer of the cold water layer is that is there the thickness varies from 1 to 100 micron, Beilby layer to 1 to 100 nanometer then, oxide layer 1 to 100 nanometer and then the physics of layer dime dimension is very less, it is just on the surface, I do not know 1 nanometer.

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Now, finally, just if you think about different properties which are dependent on surface, they may be categorized into 3 types, physical properties, mechanical properties and chemical properties. Physical properties like roughness and color they are dependent on the surface, mechanical properties like micro hardness, rupture strength, fatigue and wear properties and chemical properties like corrosion and high temperature oxidations, which are dependent on the surface.

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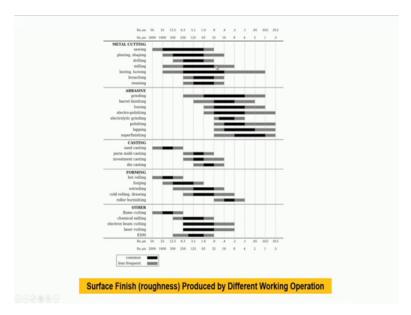
So, in the next few slides, I will discuss about the different physical properties and their role. So, if you talk about roughness, roughness is nothing but, the radiation of the unevenness of the surface as compared to that of that of it is ideal and ideal the ideal surface actually but, actually what you see that ideally no surface is roughly. So, actually so, there is always certain degree of unevenness on the surface. So, these unevenness is created because, of if you talk about that atomic level unevenness, you can understand it from KLK model TLK model, where you saw that again in atomically also, surfaces are not ideally smooth in nature.

So, but on the other hand, if you do different working operation, they are also different kinds of odd evenness is introduced on the surface. So, the unevenness on the surface is because, of the or maybe you can say micro scale unevenness on the surface is because, of the working operations, the surfaces faced. The unevenness may be categorized into different in different terms, based on the scale at which you are observing like surface roughness, surface waviness, lay surface with cutoff, waviness height.

So, these are the different terms which are actually employed to define the surface roughness. So, surface roughness is we find, when you talk about roughness it is nothing but, it is the degree of unevenness in is very smallest dimension and usually roughness is measured by contact or non-contact profilometer and there it is measured in terms of average roughness, that is the distance between the top surface and that of bottom or maybe you can also measure it in terms of the RMS roughness. So, these 2 terms are used to define the surface roughness and waviness is nothing but, this is again the roughness of the material at a scale larger than the smallest scale.

So, this is generated because, of the different working operation. So, surface where surface loses it is straightness. So, you call it waviness. So, waviness width is again a kind of smallest dimension, where the waviness is observed and the dimension of the roughness along which roughness is generated is called lay and they had maybe lot of flaws on the surface because, of different different generation associated with processing.

So, this is very important. So, if you talk about the roughness and it is important roughness is not really because. of the surface energy but, it is the fact and phenomena, to some extent associated with surface energy, as you saw in the surface atomic arrangement, to some extent it is generated because, of the processing operation, the surface has undergone and as a result of which many properties are actually influenced like lustre is influenced by surface roughness, friction coefficient is influenced by surface roughness, wear is influenced by surface roughness, corrosion resistance is influenced by surface roughness, lustre is influenced because, higher is the roughness, higher will be the scattering sides, as a result of ways surface loses it is reflectivity, lustre is lost, coefficient of friction also increases as the roughness is increased, wear value as a result of which increases, corrosion resistance is influenced because, higher is the roughness more will be the exposed area and as a result of which naturally corrosion will be higher. So, these are the different properties, which are influenced by surface roughness.

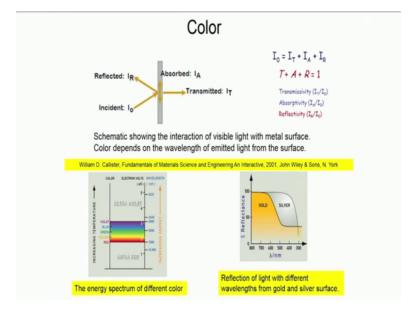


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And, this is the slide which shows there different roughness value, basically related to different processing operation. So, you can understand that different cutting, casting the processing like melting casting, different types of roughness is different values of roughness is generated, if you talk about invest investment casting.

Then roughness level is much lower than that of sand casting, if you talk about different cutting or machining operation, you will find that lapping or policing induces much lower roughness than that of grinding and cutting also you will find that by sawing you have very high roughness on the other hand, very boring milling, roughness level is reduced. Similarly, same cutting or offers very high roughness, EDM cutting offers quite low roughness. So, different levels of roughness is generated because, of different

working and processing operation, if you are interested to maintain the roughness to a very low value, you have to choose the processing operation accordingly.



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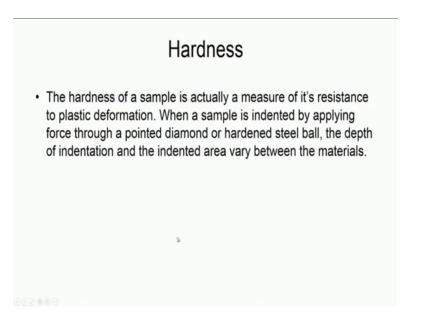
So, that another important properties which is influenced or dependent on the surface is the color of the material. So, color depends on that response of the materials towards visible light. So, if you see the metallic materials, they are mostly colorless in nature because, in the metallic materials there is overlapping between various band and conduction band.

So, electrons which are basically, which absorbs most of the energy is associated with the typical visible light, they all deflects it back and as a result of which there is no very less amount of energy is absorbed and all the energy is associated with the different wavelengths of visible light, they are basically reflected back, as a result of which you will find colorless in nature. On the other hand, some of the metallic materials like gold and copper, they are having large numbers of electrons in their d vents. So, d levels electrodes are there; so, as a result of which, basically when the visible light is exposed onto the surface.

They basically they are the different atoms different electrons, absorbs different types of different levels of energies and as a result of which you will find that when they reflect, the maximum energy is which are emitted depending on that, the color varies actually. So, we will find that gold's are mostly yellowish in nature, which is having the

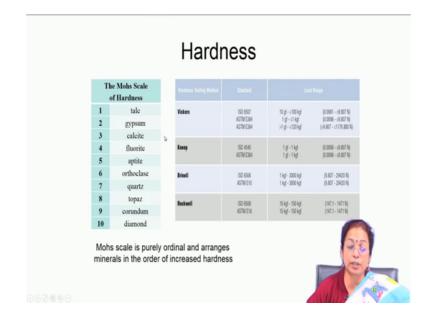
wavelength in the range of 7000 to which is having wavelength in the range of 6000 to 6500 Angstrom, nanometer on the other hand, you will find that if you talk about the silver and then iron, they basically reflects most of the electrons, I mean most of the energies. So, they are basically whitish in nature. So, depending on the electronic configuration, you will find that the energy will change. So, this particular thing again is dependent on the surface because, surface is exposed to the visible light.

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And, you will find that, if you are interested to colorize the surface, you have to form the compound layer on the surface of the metal, by exposing it to different environment and there are different ways by which you do that to. So, we will discuss about these different techniques, when you discuss about the conversion coating chemical as well as electrochemical conversion coating then, if you talk about mechanical properties hardness is one of the important mechanical properties which come into picture. So, it is nothing but, it is the measure of it is resistance to plus plastic deformation. So, basically it is measured by indenting it with a, indenter and subsequently measuring the size and shape of the indentation mark.

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And, there are different scales by which hardness is actually represented like the Vickers scale, Knoop scales, Brinell and Rockwell scale, it is dependent on the there is also a small scale a of hardness measurement which is nothing but, the ordinal scale, where the relative scratch ability of different minerals are basically sequentially placed and more scale level statements, it is the diamond highest hardness and level one is talc which is having lowest hardness but, this is as I mentioned you know this is the ordinal scale. So, you cannot really say, which one is having how many times higher hardness then that of the below 1.

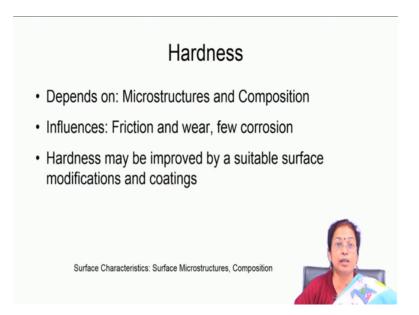
So, like diamond to corundum if you see the hardness of diamond it is. So, types that of corundum on the other hand, if you talk about the corundum on topaz, it is again 2 times that of hardness of topaz. So, it is really relative scale and like that there are several other small scale of several different minerals as well.

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This is the earliest way of representing hardness but, now there are different scales or different ways by which you measure hardness, it is very much dependent on the micro structure and composition of the different materials actually. So, if you talk about the iron and steel, it is having hardness varying from for example, 100 v chain or hardness a 100 days b to, 700 hp and it is called, if it is copper and it is alloys it is having quite a low hardness. So, if it is aluminum and alloy it is having even much lower hardness.

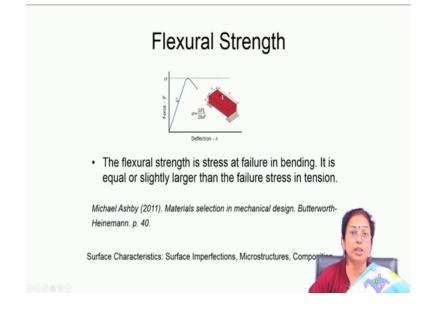
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So, usually pure metal is having lower hardness and you can harden it by different hardening operation like strain hardening, grain define when induction, strain hardening then grain refinement precipitation hardening, edge hardening, where different operations you can increase the hardness to a large extent. So, hardness is again a kind of primary mechanical properties which, influences many important surface dependent mechanical properties like friction and wear, corrosion property and it is dependent on the microstructure and composition of the materials and it is also dependent on the surface structure because, if you do any kind of operation on the surface, the hardness will also vary particularly the scale of hardness will vary.

So, if you measure the half hardness in nano scale, with the help of nano indentation technique, you will find that the hardness of the surface is much higher than that of hardness of the bulk of the material because, of the presence of work hardened layer or oxide layer all the Beilby layer. But, on the other hand, if you measure it on my micro scale and also in macro scale, you will find that effect of surface natural atomic arrangement or natural change in structure because, of the surface energy, it is not visible in the hardness value, you will get the informations about the bulk hardness of the material, which depends on the microstructure and composition of the material itself.

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Flexural strength is another important mechanical property, which is dependent on the surface which is nothing but, gives the information about the failure in bending.

So, this is dependent on the surface because, often failure starts from the surface flaws surface impurities, where stress concentration is much higher. So, it is also taken as the property which is dependent on the surface so, if you just improve the surface finishing or maybe, if you increase the surface hardness to a little extent, you can increase the flexural strength to a large extent.

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# Summary

- Importance of surface
- Surface Energy
- Surface Dependent Physical Properties
- · Surface Dependent Mechanical Properties



So, in this particular talk we discussed about the importance of the surface, the surface energy the phenomena related to surface energy and the properties influenced by the surface energies, we also discussed about surface dependent physical properties and primary mechanical properties like flexural strength and also hardness.

And, other important mechanical properties which are dependent on the surface like, the wear resistance and also fatigue property that will be discussed in the next few classes and surface dependent chemical properties like, corrosion and high temperature oxidation, will also be discussed in the next 2 classes.

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Thank you very much.