

Surface Engineering for Corrosion and Wear Resistance Application
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Lecture - 05
Surface Properties – due to mechanical activation

Welcome to the 5th lecture of this Surface Engineering course. We have already had discussion on structure of solids on the evolution of microstructure we discussed about the different defects possible in crystalline solids. And also discussed the evolution of surface or the reason why surfaces are always inseparable from any solid and what are the influences surface can play on various properties of solids.

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Surface Engineering – Panoramic View

Engineering solid: Pure (Metallic/Polymeric/Ceramic) + Composite or Real (crystalline and amorphous) – **Bulk + Surface** (inseparable)

Surface: Structure, Characteristics, Composition, Energy, Properties

Surface dependent properties: Mechanical (hardness, wear, friction (mechanical), corrosion, catalysis, oxidation (chemical), adhesion, reflectivity, emissivity, optical (physical))

Engineering consideration: Design, Life, Performance, Safety, Reliability, Aesthetics, Quality, Cleaning, Environment, Modeling

Surface engineering techniques: Coating, Cladding, Plating, Deposition, Thermal/chemical treatment, Polishing/grinding, Implantation, Diffusional treatment, Surface melting/alloying

Concerned application: Mechanical, Electrical, Tribological, Magnetic, Catalytic, Energy, Electrochemical, Degradation/protection

Concerned industry: Manufacturing, Automobile, Aerospace, Power/energy, Chemical/petrochemical, Biomedical, Textile, Defense, Food packaging, Machine/heavy industry, Mining, Electrical/electronics

Today we are going to discuss about the surface dependent properties the overall spectrum of surface dependent properties and how actually they can be classified and what role do they play in determining the overall performance of any engineering solid. We already have discussed that engineering solids actually can be divided into the three pure classes of metallic, polymeric and ceramic and combination of any of these which actually is more often than not found in reality.

So, we never get all metallic or all polymeric or all ceramic we possibly in a real life application a component will have input from various kinds of materials of different origin. We also know that they could be either crystalline or non crystalline, but what is

most important is that whenever you we talk of a solid, it will have a definite volume and a boundary and beyond the boundary or at the boundary we certainly invoke the concept of surface.

So, bulk and surface are inseparable. We discuss the structure of surfaces the different characteristics associated with them the different types of surfaces of the reason why surface energy is associated with different surfaces and how energies can be different and how different energies can also manifest itself into different types of properties.

Now, what is property? Many times whenever we talk about properties we all tend to you know express as if property is something which is always understood, but then how does one define the notion called property. Property is nothing, but its essentially the reaction to certain activation this. Let us say if we try to deform a material and we cannot then we say the material is very strong or hard that is because we are trying to apply mechanical forces and expecting deformation. And if it does not deform, then we immediate reaction is that the material must be very hard as strong. Similarly, if something is very soft and pliable we say this is very soft because mechanical activation can easily deform it.

So, likewise we can say that when electrons flow very easily when certain potential difference is applied we immediately say that the material is electrically conducting or otherwise we say its insulating and so on and so forth. So, essentially reaction to the external stimulation is property. Now there are host of properties which essentially are connected with the bulk of the material whereas, in this course we are dependent we are concerned with the surface dependent properties and we can divide them into certain groups we will come to that in more details very soon.

But the question is why are we interested in surface dependent properties because there are very many engineering considerations for example, a design engineer needs to know how a surface will behave under certain activation in certain environment. In order to predict the life we have to worry about the surface condition and interaction of the surface, the overall performance the safety and reliability issues of any engineering component particularly under mechanical activation, but even under very high applied voltage or various kinds of activation.

We need to understand the safety and reliability and efficiency of performance. The aesthetics depends on surface the quality overall depends on surface if you need to clean

we have to worry about the characteristics of the surface the interaction with the environment and finally, for any kind of modeling of the behaviour of a material under given condition and environment. We need lot of input about the surfaces and the interaction of surface with various kinds of environment.

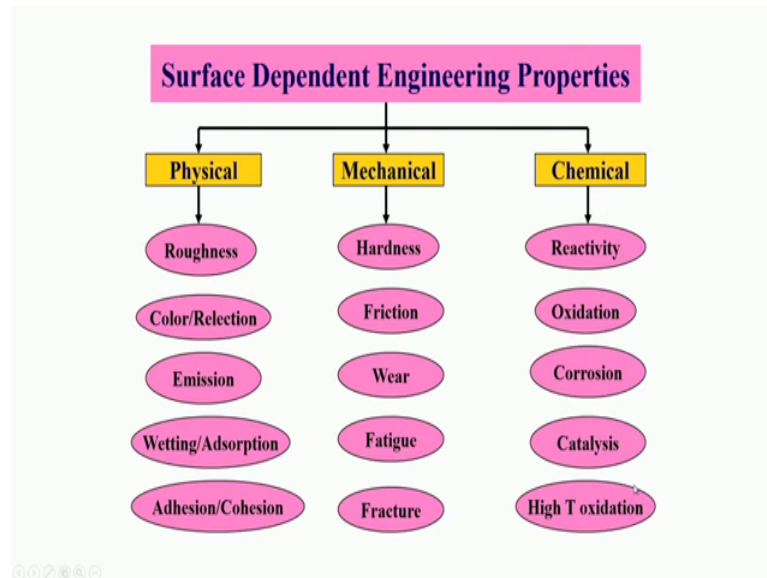
We actually intend to understand how can we modify the near surface region which could be in the limit just a few atomic layers and on the extreme could be several millimeters. So, in this entire range of the surface if we can change the microstructure and composition or either of them, we certain can improve many of these properties that we just discussed about.

So, the techniques which allow us to tailor the surface dependent properties namely the microstructure and composition are called surface engineering techniques and there are very many of them will the entire course is devoted to that. So, we will be discussing more in details of those where do we apply the surface engineering knowledge we apply for various kinds of mechanical devices, electrical devices, tribological applications magnetic catalytic energy or power generation electrochemical phenomena various kinds of degradation and protections required under various atmospheres or service conditions.

So, in all these applications surface engineering or surface dependent properties surface characteristics all come very handy and essential, but the most important part is that there are almost all kinds of industries they certainly need they certain concern surface phenomena or surface dependent phenomena and they certainly worry about the overall performance of the component and hence they need to worry about their surfaces as well.

So, it can be just from very integrate to mundane routine manufacturing processes automobile industry aerospace power or energy production chemical or electrochemical, biomedical, textile, mining industry, heavy machine, food packaging, electrical electronics almost all kinds of applications wherever we are dealing with a hardware which is essentially a solid component. We certainly will have surfaces and these surfaces are very very important to make sure that the component actually performs to our desired expectation.

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So, talking about surface dependent properties essentially we are talking about engineering properties for example, when we talk of strength when we actually perform tensile deformation or a compressive compression deformation or torsional we are talking about the strength of the bulk. But when we try to scratch a solid and see that whatever device, we are using for scratching is unable to make a scratch then we conclude that the surface is very hard and we cannot make any scratch or indentation.

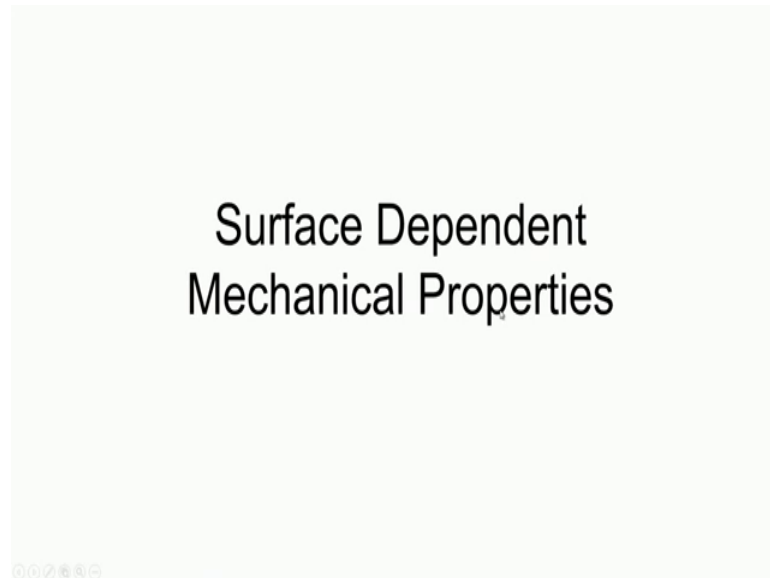
So, we then derive a property called hardness and which essentially means that the component is very much resistant to surface deformation. So, likewise I have taken the liberty of just speaking up three classes of properties namely the physical, mechanical. And chemical and listed certain properties as for example, which are essentially dependent only on the surface chemistry and surface microstructure.

For example, the roughness asperities on the surface the colour and reflection the emission or emissivity the variability or adsorption characteristics adhesion or cohesion all these properties are essentially surface dependent properties and physical in nature. When you actually apply mechanical deformation or mechanical activation then you worry about or then you are concerned with certain responses and these responses could be hardness or friction or wear or fatigue and fracture and so on and so forth.

I must also qualify that fracture and fatigue are not entirely surface dependent properties, but the failure from these two classes essentially initiate at the surface. So, in order to

improve upon the fatigue or fracture characteristics one does take care of the surfaces. Similarly chemical properties namely the reactivity, oxidation, corrosion, catalysis, high temperature, oxidation all these properties are essentially surface dependent properties.

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So, for the time being let us focus on the mechanical properties. So, essentially the definition or the scope here is that we are applying mechanical forces onto a solid component and under that mechanical activation or stimulation how does the component respond.

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Hardness

- ❖ **Hardness** is resistance to indentation
- ❖ It expresses how resistant solid matter is to various kinds of permanent shape change when a compressive force is applied
- ❖ Macroscopic hardness is generally characterized by strong intermolecular bond
- ❖ Deformation behavior of solids under load is complex and varies in different types of solid
- ❖ The genesis/origin of hardness is the bonding of aggregate, structure and arrangement of atoms
- ❖ **Measuring hardness:** Three main types of hardness measurements are done: **scratch, indentation, and rebound**. Each type may have its own measurement protocol and scale. Empirical relations exist to convert one type of hardness to another type/scale



Universal indentation hardness

So, that is the mechanical response or mechanical properties. Obviously, the first and foremost would be the discussion on hardness whenever we talk of the mechanical strength of a material even though it is surface dependent property, but; obviously, we first would like to refer to hardness. So, its nothing, but resistance to indentation or surface deformation.

So, its it basically expresses that how resistant them solid is to such attempts to deform and these deformations are usually through compressive forces and how does the material resist can he attempt to deform under such compressive loading. The hardness if it is actually can be ascertain by whatever changes the activation makes onto the surface by macroscopic observation we call it macroscopic hardness..

So, typically the so, called the Brinell hardness tester would be one such device or the rebound hardness by Poldi and so on. So, essentially they test the intermolecular bond strength of the molecules or surface or the atoms at the surfaces. But then we must realize that no matter what kind of load we apply we actually can always have certain derived component which could be tensile in nature or shear in nature and so on.

So, the application of the load may be simple, but the reaction or the act the action on to the solid can be fairly complex and that also varies in different types of solids. Say for example, the same load applied on a on a elastomer and thus a may may actually allow the formation of the elastomer, but the same load may be completely inconsequential for a hard metal or a ceramic component..

So, this the so-called hardness essentially originates from the bonding characteristics and structure and arrangement of atoms at the surface and as I said we actually can we usually express hardness in three possible ways and these three ways are related to the means and mechanism by which we apply the load. So, it can be a scratch hardness it can be an indentation hardness or a rebound hardness see samples could be different, I mean it may not be of very flat and uniform geometry it may be irregular it may be circular it may be completely brittle or powder type of materials or for example, a stone or a mineral on the other hand you can also have a very nice diamond coated surfaces.


So, various solids actually present themselves in various form and we should have a recipe for measuring the hardness for all such solid components under different conditions.

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Friction

❖ **Friction** is the force resisting the relative motion between solid surfaces, fluid layers, and material elements sliding against each other.

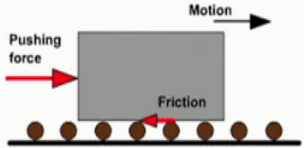
❖ When surfaces in contact move relative to each other, the **friction** between the surfaces converts kinetic into thermal energy (rubbing of wood/stone sparks fire)



- ❑ **Dry friction** resists relative lateral motion of two solid surfaces in contact
- ❑ **Fluid friction** occurs between layers of a viscous fluid that are in relative motion
- ❑ **Lubricated friction** is a kind of fluid friction where a lubricant separates two solid surfaces
- ❑ **Internal friction** is the force resisting motion between the atomic layers/planes making up a solid while it undergoes deformation

Applications of friction:

- Automobile brakes
- Friction between the head of a matchstick and the surface of the match box



If this the friction we tend to believe that friction actually works against the interest of humankind, but if there is no friction then we cannot walk then an automobile cannot stop or an aircraft cannot land after the flight. So, friction is essentially a resistive force between two surfaces in motion in relative motion and the two surfaces would be two solid surfaces or two fluid layers or essentially any two entities which are in relative motion or sliding past each other.

So, when we actually use the friction for example, when we rub wood or stone against each other we actually convert the mechanical energy to thermal energy and that is what can actually even create a spark if not a fire. So, friction also allows conversion of energy from one form to another. Now in terms of friction actually there are these four varieties which are commonly encountered we can have dry friction when we do not have any lubricant and usually we this kind of a dry friction can lead to very substantial amount of material loss or where.

We can have fluid friction which essentially can happen between two highly viscous fluid layers which are in relative motion we can have lubricated friction where we may have solid surfaces, but separated by a thin layer of lubricant which is a very common experience whenever we think of a ball bearing assembly or various other rotating parts.

We can also talk about internal friction now this is something which is not visible by our by our naked eye essentially it means that when we try to deform the material tends to

resist that the tendency for deformation and this resistance comes from the internal friction which in two term means that the amount of shear stress at dislocation requires to be able to move on the slip plane.


So, unless we actually apply sufficient load converted into stress, converted into shear stress on a particular section or a plane, which is enough for a dislocation to move unless we cross that threshold. So, called critical resolved shear stress there will be no motion of dislocation and we would say that internal friction is so, high that we are unable to deform.

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Lubrication

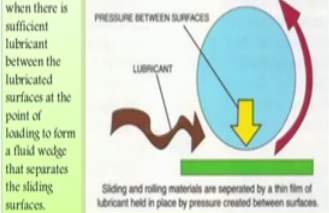
- ❖ **Lubrication** is the system applied to reduce friction between, and wear of one or both, surfaces in proximity and moving relative to each other, by interjecting lubricant in between them.
- ❖ The **lubricant** can be a solid, (e.g. molybdenum disulfide), a liquid such as oil or water, a liquid-liquid dispersion (e.g. grease) or a gas

Hydrodynamic Lubrication



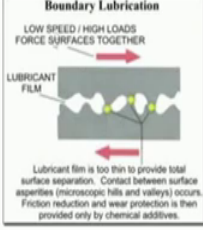
hydrodynamic film occurs when there is sufficient lubricant between the lubricated surfaces at the point of loading to form a fluid wedge that separates the sliding surfaces.

Full Fluid Film (Hydrodynamic) Lubrication



Boundary Lubrication

LOW SPEED / HIGH LOADS FORCE SURFACES TOGETHER




So, when you know that two solids when they rub against each other are likely to cause certain reaction forces and eventually will lead to continuation of applied energy, you would like to reduce that and how do you reduce? You apply lubricants. So, lubrication essentially is essentially a system in which you try to reduce the friction and wear or both and this is by applying certain extraneous agent which can be solid.

For example, molybdenum disulfide can be liquid like oil or water or some other liquid or it could be a liquid liquid dispersion. Say for example, two immiscible liquids together and they when they are under force they actually allow easy sliding between them, you can even use certain gas or vapour for the purpose of lubrication. So, the whole purpose of lubrication is to reduce the friction and also to make the deformation process or mechanical motion easier.

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Wear or Abrasion

- ❖ **Wear** can be defined as a process where interaction between two surfaces or bounding faces of solids within the working environment results in dimensional loss of one solid, with or without any actual decoupling and loss of material. Wear is erosion or sideways displacement of material from its "derivative" and original position on a solid surface performed by the action of another surface.
- ❖ **Stages of wear:** Under normal mechanical and practical procedures, the wear-rate normally changes through three different stages:
 - **Primary stage:** surfaces adapt to each other, wear-rate varies from high to low.
 - **Secondary stage:** a steady rate of ageing is in motion.
 - **Tertiary stage:** components undergo rapid failure due to a high rate of ageing.



Rear sprocket for a bicycle where the left one is unused and the right is worn

- **Adhesive wear:** Unwanted displacement and attachment of wear debris and material compounds from one surface to another.
- **Abrasive wear:** occurs when a hard rough surface slides across a softer surface.
- **Erosive wear:** Caused by the impact of particles of solid or liquid against the surface of an object.
- **Corrosion and oxidation wear:** Due to chemical reaction between the worn material and the corroding medium.

Another very commonplace mode of deformation and degradation under mechanical activation is wear or abrasion. So, here again we are talking about relative motion between two surfaces and when we actually have such relative motion then we expect that there will be certain amount of resistance to default to sliding motion. And that is primarily because of the fact that all solid surfaces which are synthetically produced or manufactured by some artificial means will definitely carry certain amount of asperities or roughnesses.

Now, when we have two surfaces with two different degrees or similar degrees of surface roughness they are bound to the tips of these asperities are bound to interact with each other and then try to resist the relative motion. In most of the cases when we deal with surfaces which are dissimilar in terms of mechanical properties or hardness then at least then we can easily identify which one is harder than the other.

And the harder surface actually will cause more damage to the software one. Even if two surfaces are of similar mechanical properties and surface asperities or contour, even there we because of the application of forces a component derived component of that could be compressive in nature and as such derived compressive loading there could be momentary welding of two asperities at least the tips of the asperities and the subsequent fracture of such coal welded bonds.

So, in the process a portion of the material will be dislodged and that is the particle or that is the volume of the material which is lost in the process and called a worn debris. So, no matter whether its a dry or lubricated condition where as a function of time under the comparable condition or under the say at room temperature not at elevated temperature.

Will always see stages of where the primary stage where asperities will interact with each other and wear rate can be anything from very high when you have very large asperities and very hard and brittle surfaces to very low when you have relatively flat surfaces.

But this is the stage when the two surfaces actually try to eventually become compatible with each other. So, when the asperities are lost the surface roughness is reduced and then they become flatter and become a closer to each other. The second stage or the secondary stage is when we actually hit upon a steady state so; that means, now the friction is reduced and maintains a steady state level as a function of time.

And in the tertiary stage again the friction goes up and we actually that is because by then we would have accumulated sufficient amount of debris and for whatever reason there could be accelerated this accelerated loss of material from the surface, but all these processes of primary, secondary, tertiary and so on they essentially depend upon the application of the load the degree of loading the contour of the two surfaces the presence or absence of lubrication the speed at which the two surfaces are gliding past each other or rotating against each other and so on and so forth.

See for example, if you think of a the rear sprocket of a bicycle. So, in fresh condition they are very geometric and nice and absolutely without any blemishes, but after a certain number of rotations against the chain you would expect some amount of wear. And you can easily make out that this particular sprocket probably was rotating in clockwise direction and as a result the tip underwent certain amount of wearing because of which it is now fairly deformed and also it has lost certain amount of materials from the tip..

So, this kind of wearing or abrasion actually can happen because of adhesive wear, because of abrasive wear, because of erosive or corrosive and oxidative wear. So, in case of adhesive wear what I was saying just a few minutes ago, that we actually anticipate

that there will be some amount of temporary bonding between the surfaces or forces of a abrasion followed by dislodging of those bonds and in the process we lose some material from either of the surfaces.

In abrasive where we are encountering a situation where we have harder surface or harder particles which are sliding against a softer surface leading to certain loss of materials. In case of erosive wear or erosion, we actually expect stream of particles flowing with either solid or liquid onto the surface.

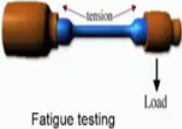

So, for example, it can be a slurry which is hitting a drum or a rotating drum or maybe a feeder chute where its causing a very high amount of damage because of two reasons irregular shape of the particles which are being harder than the surface and more importantly the velocity and the momentum with which they are hitting the surface. So, this actually can be fairly localized damage it can lead to very localized damage and can be extremely harmful.

We also may encounter situation where presence of corrosive environment or oxidation or high-temperature and in air together can actually accelerate the damage already occurring due to wear. So, where occurring in corrosive or oxidative environment can be more accelerated and actually can cause greater damage.


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Fatigue

- ❖ **Fatigue** occurs when a material is subjected to repeated loading and unloading. Thus fatigue weakens a material by repeatedly applied loads.
- ❖ Fatigue usually occurs under **tensile** stresses but fatigue cracks may occur due to compressive loads too
- ❖ The greater the applied stress range, the shorter the life.
- ❖ Damage is **cumulative**. Materials do not recover the state of stress when rested.
- ❖ **Fatigue life** (N_f) is the number of stress cycles of a specified character that a specimen sustains before failure of a specified nature occurs. For some materials, notably steel and titanium, there is a theoretical value for stress amplitude below which the material will not fail for any number of cycles, called a **fatigue limit**.
- ❖ Fatigue life is influenced by a variety of factors, such as *temperature, surface finish, metallurgical microstructure, presence of oxidizing or inert chemicals, residual stresses, scuffing contact (fretting)*, etc.
- ❖ Fatigue cracks that have begun to propagate can sometimes be stopped by drilling holes, called drill stops, in the path of the fatigue crack (**Griffith's law**).



Fatigue testing



Drill stop: Bridge rescue

Another kind of damage that we often encounter under mechanical activation is fatigue now here the application of load is of slightly different type and this loading is essentially repetitive in nature or cyclic in nature. So, the amplitude of the loading can be equal on the positive and the negative cycle or can be non equal, but what is important is that the load is applied in a cyclic manner.

So, whenever we see such cyclic loading essentially we are the material the solid component is to experience loading and unloading cycles and in this kind of a situation almost all engineering materials are known to fail at a level which is lower than the ill strength. So obviously, that when a designer designs a component only based on the yield strength or the tensile strength or compressive strength for that matter.

Then that may not be adequate because if the material if the component is likely to undergo repeated cycles of loading and unloading then the material eventually may fail at a level of stress which is lower than the design limit. So, one has to take care of not only tensile or compressive component of loading, but also check out whether we expect fatigue or cyclic loading condition.

So, in such condition whenever we actually encounter such cyclic loading condition what one needs to be very careful about is to figure out whether we have a discontinuity already existing for example, a crack or a dent or some kind of a scratch existing on the surface with the sharp tip and if the surface is experiencing tensile loading.

We all know that the whenever we have a crack or any amount of discontinued on the surface under tensile loading they actually are likely to undergo accelerated failure or accelerated crack opening. So, what is important is that the overall condition on the final surface on the external surface if it is tensile in nature then damage due to fatigue can be more harmful or more likely. So, in order to prevent our arrest we would like to create solid components which are undergoing repeated cyclic loading or deformation.

For example, a gear or a rotor or a blade or rotating blade or a turbine or shaft in all such cases if you would like to actually create a situation where the state of stress on the surface should be compressive in nature and not tensile. So, that even if a crack initiates the crack first has to overcome the loading which is towards each other as is expected in compressed loading and then first have to work on this compressive loading and then go into tensile regime and then only the crack can open.

So, anyway therefore, the designers what is important is to determine this fatigue life and fortunately for metals you actually can define what is known as endurance limit which essentially says the number of cycles the which essentially defines the stress amplitude or the minimum stress amplitude which a material can withstand no matter how many cycles of loadings are applied.

In other words if you are applying load below the endurance limit then in metallic systems one can go even up to infinite number of cycles and still the material is not supposed to fail due to fatigue. But situation in case of ceramics or non metallic systems is not so simple. So, you do not see an endurance limit curve which is flat flattening and becoming horizontal at the end, but the curve can actually continue to move downward. So, there you have to apply a separate type of criteria for defining the fatigue limit.

So, this is important for a designer to understand what would be a fatigue limit. So, similarly we actually fatigue limit is also or life is also influenced to a large extent by the temperature, surface finish, the microstructure, the surface, the environment and also the kind of residual stresses which are existing on to the surface. And in case of such fatigue crack growth one actually can invoke the Griffith's law and understand that if there is a sharp crack which is approaching which is opening up onto the surface somewhere.


If you create a circular hole in front of it then you expect that the crack growth will be arrested because of this Griffith's law. We know that the stress maximum for an applied for an applied load or a stress the crack the crack-tip experiences much higher stress. And that maximum stress at the crack-tip is inversely related to the square of the radius of curvature of the of the discontinuity ahead.

So, if you make a circular hole since that the radius is extremely large compared to a sharp radius of a sharp crack tip in such a situation, you would definitely expect the crack to get arrested because of the intervention of this circular hole ahead of such a crack tip.


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Fracture

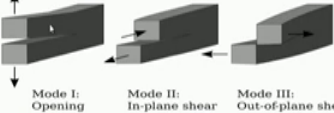
- ❖ **Fracture** is the separation of an object or material into two or more pieces under the action of stress.
- ❖ Fracture occurs when certain **displacement, discontinuity or crack** develops within the solid that eventually reaches the surface.
- ❖ If a displacement or crack develops perpendicular to the surface, it is called a normal **tensile crack** or simply a crack
- ❖ A displacement developed tangentially to the surface of displacement is called a **shear crack, slip band or dislocation**.
- ❖ **Fracture or breaking strength** is the stress at which a specimen fails or fractures.
- ❖ The fracture is termed **ductile** or **brittle** depending on whether the elongation or deformation is large or small



Brittle fracture in glass



Ductile fracture of a specimen



Mode I: Opening Mode II: In-plane shear Mode III: Out-of-plane shear

Finally, material can fail when it fails particularly for brittle materials we invoke the concept of fracture. Fracture is not necessarily a surface dependent properties, but we must realize that essentially the material fails only when the crack opens up to the surface. So, that is where you again have a major role of the surface and you would like to create the surface or modify the surface microstructure composition or the state of stress such a way that any crack even if it forms and opens and reaches the surface is not able to propagate very easily.

But when we talk of fracture we have to realize that there could be various types of modes of fracture for example, if the crack growth is perpendicular to the direction of application of load then we call it mode I fracture similarly there could be mode II whether the crack opening direction is parallel to the load application direction. But it can be in plane or out of plane mode and accordingly the various types of fracture can happen in solids.

But essentially the broad classification would be that engineering solid could either be ductile where the where the crack is unlikely to form very easily and propagate very drastically on the other hand there could be a brittle fracture which actually can lead to formation or propagation of the crack, but easily.

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Points to ponder (recapitulation):

1. How can you define and classify surface dependent properties?
2. Where are such surface dependent properties important and why?
3. What are the surface dependent mechanical properties?
4. How do such surface dependent mechanical properties affect life and utility of solid components?
5. What are the equipment, protocol and units for the assessment of surface dependent mechanical properties?

So, its time to now take a look at or summarize what exactly we have discussed so far. So, we made an attempt to understand what our surface dependent properties and where do they come from and we try to classify them into primarily 3 major baskets of physical, chemical and mechanical. I try to give you several examples as to why surface dependent properties are very important for various aspects of design life assessment synthesis or fabrication of components and so on.

And surface dependent properties could be of various types, but then when you talk of hardness or friction or where and so on. I explained that these are essentially mechanical properties surface dependent mechanical properties because all these properties are essentially response to simulation which is mechanical in nature. They certainly affect the overall life and utility of solid components the surface I mean mechanical stresses applied onto the surface.

So, we need to understand how do they where do they arise from and how do how are they affected and how can we actually improve upon by either changing the microstructure or composition or state of stress on to the surface. And finally, we also need to understand that when we want to measure the hardness, what are the equipments available to us, what are the units of hardness or for defining wear, what are the different types of wear, what machines do we use and how do we express the kinetics of where or for example, friction and so on and so forth.

So, that these are assessed in a typical as a typical engineering property which can be used and utilized for various design and applications.

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Thank you very much.