Medical Biomaterials
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Lecture – 27
Metallic biomaterials

Hello everyone, welcome to the course on medical bio materials. We will continue on this metallic bio materials let us recap what we did on this. First we looked at what is miller index of a plane, it means a plane has an unique identity which is represented by this miller index.

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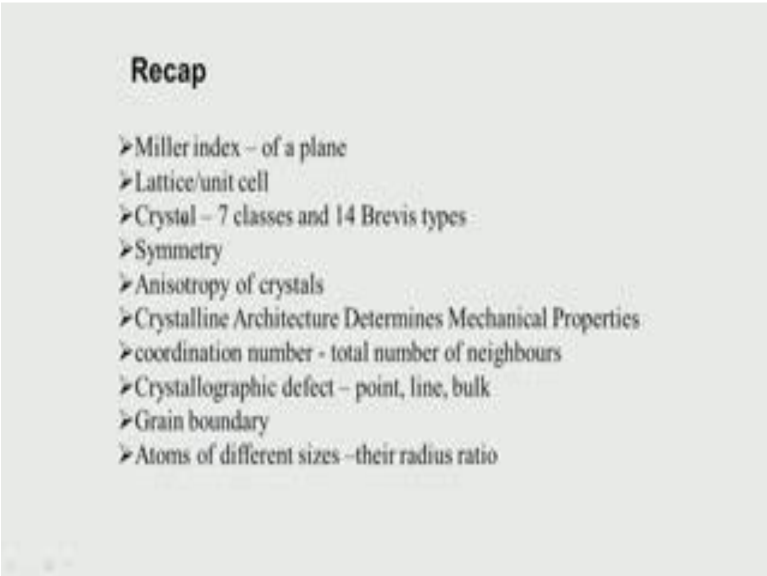

Then what is this lattice unit cell; that means, each crystal is made up of certain repeating units infinite repeating units and that is called a unit cell there are 7 classes of these unit cells and then there are 14 Brevis types.

So, we looked at 7 classes of unit cells based on the 3 sides A B C and based on the 3 angles alpha beta gamma then we looked at the symmetry there are different types of symmetry that is the translational symmetry, rotational symmetry, mirror symmetry and so on, why do we have to do all this because there is an isotropy of the crystals; that means, the direction in which for example, the load is acting the number of atoms in that crystal will be part of it. So, that will affect the mechanical properties. So, for example, if it is a bcc and the direction of the force is across the longer diagonal the; and BCC, the atom that is inside the body also will be part of it. So, the mechanical strength will be higher the Young's modulus will be higher where as if the load is along one of the planes that particular atom which is inside the bcc will not be taking place. So, the number of atom comes down. So, the Young's modulus also decreases so and so on actually.

So, the mechanical properties are determined in the direction in which the force acts for a bcc or for a FCC or a HCP, then we looked at something called coordination number; that means, total number of neighbours that each atom will have. So, what is the coordination number for bcc, what is the coordination number for FCC, what is the coordination number for HCP and so on and then defects because when the crystal starts growing, it is not going to be completely perfect there are going to be point defect there could be line defects there could be bulk defect there could be impurities coming into it and so on.

So, we looked at defects because defects again is going to affect the physicochemical properties of the particular crystal or the metal then we looked at grain boundary as the crystal grows from different direction they come and collide inside and there are grains formed and the grain boundaries determine the slip their defects their physical chemical properties and so on actually. So, grain boundaries are very very important and later on we are going to look at some times corrosion starts taking place along the grain boundary also.

So, grain boundary plays a very important role in the properties of the metal and then we looked at atoms of different sizes when they are part the crystals for example, sodium chloride sodium and chlorine how do they form a crystal or if I am going to add an impurity atom to the existing crystal for example, in stainless steel we are having a carbon we are having nickel with iron. So, how are they going to fit into it are they of different radius or of the; of same radius and so, what are the different sizes of atoms that could just fit into the gap left behind by other atom.

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Metal	Crystal strcuture
Cr	bcc
Co	hcp
Fe	bcc (<912oC) fcc (912-1394 bcc (>1394)
Mo	bcc
Ni	fcc
Ti	hcp(<900oC) bcc (>900oC)
NaCl	fcc
Al2O3	hcp
PE	orthorhombic

So, all these we looked at in the past 3 or 4 lectures and today also we will look at some more properties of metals. So, the crystal structure like I said chromium is a body centred cubic cobalt is a hexagonal closed packing iron interestingly the packing crystal structure changes at different temperatures at 900 less than 912, it is bcc and its FCC between 912 and 1394, it is again bcc around greater than 1394. So, if you look at molybdenum for example, it is a bcc nickel is FCC titanium at 2 different the temperature less than nine hundred its HCP above nine hundred its bcc.

Sodium chloride is FCC aluminium oxide HCP polyethylene is polymer generally polymers will be amorphous it will not be really crystalline a majority, but again there are many polymers which are crystalline or they could have a mixture of crystalline and amorphous p polyethylene is orthorhombic.

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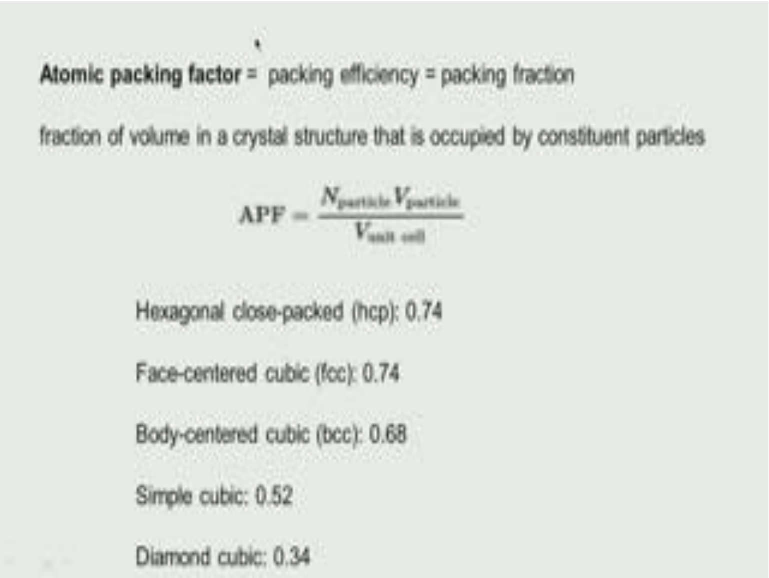

There is something called atomic packing factor, it is also called packing efficiency or packing fraction packing fraction; that means, fraction of the volume in a crystal that is occupied by the atoms; that means, the opposite of the 1 minus that fraction will give you what is a void space the void space if its minimum then it will be a very strong crystal if the void space is maximum it is like a porous. So, the strength; this is much much lower. So, the hexagonal closed packed if we take HCP the atomic packing fraction is point. So, 4 if you take face centred cubic packing fraction is 0.74, if you take body centred cubic its 0.68 simple cubic; that means, only the corner 8 are filled with atoms it will be 0.52 diamond cubic 0.34. So, as you can see it keeps going down and HCP has the highest packing factor 0.74 then comes FCC then comes bcc and so on actually, so how do you calculate?

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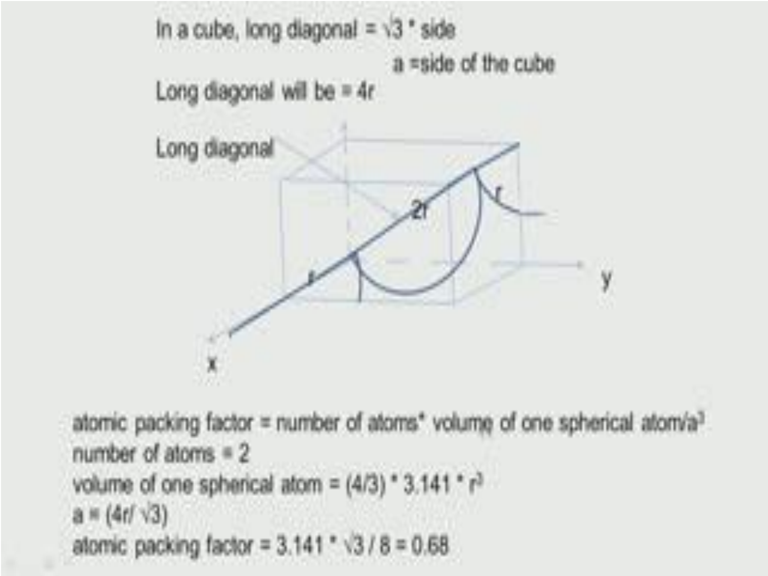

Let us take bcc for example, now we have been seeing bcc, there is 1 big atom in the centre that is why it is called body centred and then we have 8 atoms at 8 corners. So, if you take the long diagonal, we have the big atom 2 r of radius r, 2 r is the length and then another atom at the corner both the corner. So, this length is 4 r. Now for a cube the long diagonal is given by square root of 3 sides. So, if you take a as the side, square root of 3 a should be equal to 4 r, we looked at that long time back right for some other purpose also.

Now how many atoms are there number of atoms is one big atom that is part of this cube and there are 8 corners, there are atoms, but these corner atoms are shared by 8 different cubes. So, that will be one eighth of multiplied by 8 that will be 1. So, the number of atoms will be 1 plus 1 2. Number of atoms is 2 volume of 1 spherical atom 4 by 3 pi r cube 4 by 3; 3.14 into r cube.

Now, a I said is equal to 4 r by square root of 3. So, what is packing factor number of atoms volume of 1 atom divided by the volume of this cube; cube is a cube. So, a is given here. So, you can put it here that will become cube volume 1 spherical atom is this, multiplied by 2. So, when you do all this we get 3.14; 1 into square root of 3 by 8.68. So, bcc is bcc 0.68 that is how you get it. So, its lot of geometry involved in this type of calculation packing factor is very important for you to know how well packed the crystal is or what is the void space in the crystal.

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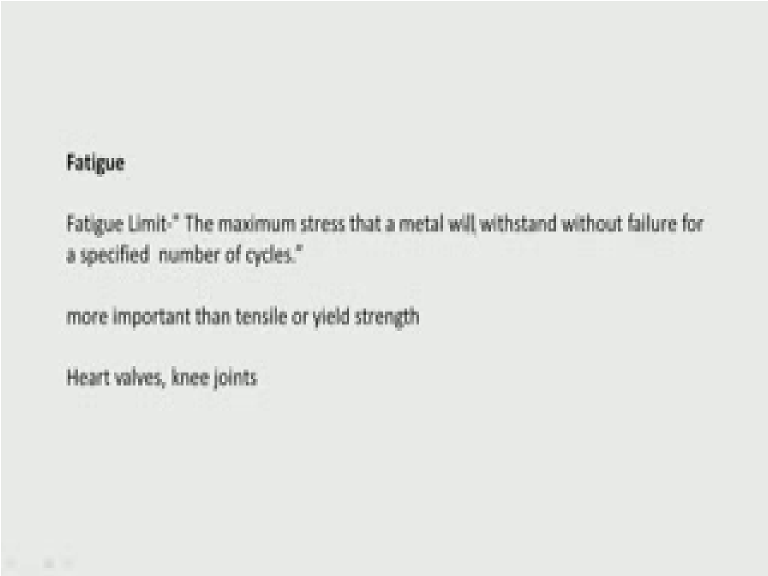

Fatigue is another important property which comes in of course, even in non metals the maximum stress that a metal will with stand without failure for a specified number of cycles for example, if you have heart valves it keeps on moving opening moving opening. So, that is how many times we can do that it is more important than tensile or yield strength because heart valves knee joints and all these undergo lot of fatigue. So, that is more important rather than the strength.

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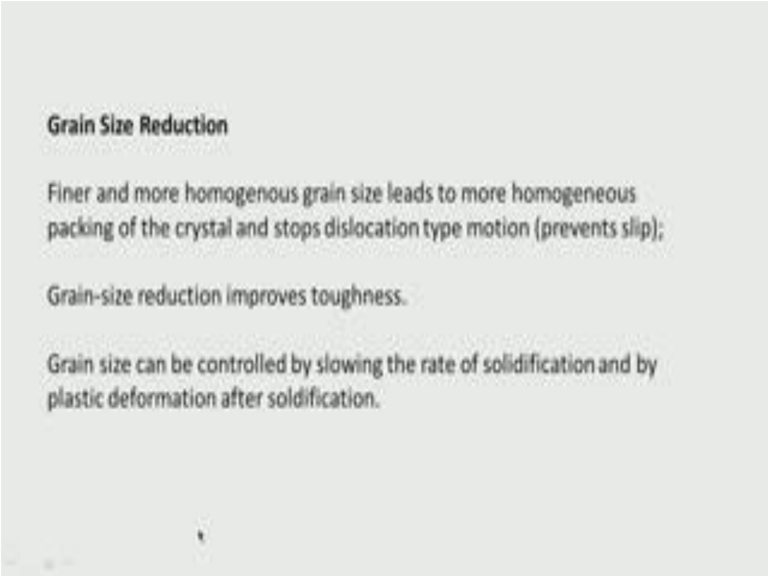

Grain size reduction like I said grain boundaries are formed because as the crystal grows from different directions and they collide and then there is a grain boundaries that are formed. So, ideally smaller the grain size stronger will be the particular crystal and finer and more homogeneous grain size leads to more homogeneous packing of the crystal and it stops dislocation type movement; that means, it will prevent slip of each crystal. So, it improves the toughness. So, ideally in metals they like to try to reduce grain sizes.

This can be controlled by slowing the rate of solidification; that means, when it is cooling do it very very slowly do not do it very fast then you will have lots of big big crystallines and there will be lot of grains plastic deformation after solidification that is you have heard of the stress strain graph we have the elastic initial and then later on we have the plastic. So, once it has cooled down and try to deform it in the plastic. So, all these will help in the grain size reduction.

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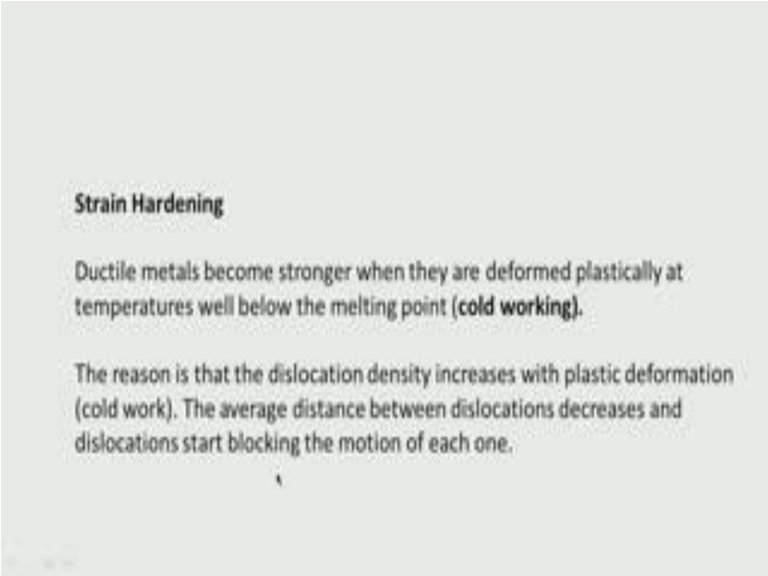

There is something called strain hardening. So, ductile metals become stronger when they are deformed plastically at temperatures well below the melting point. So, that is called cold working. So, bring it down below their melting point and then they deform it plastically. So, that it gets very hard the dislocation density increases with plastic deformation. So, the average distance between dislocation decreases and dislocation starts blocking the motion of each one. So, they are not going to get dislocated further.

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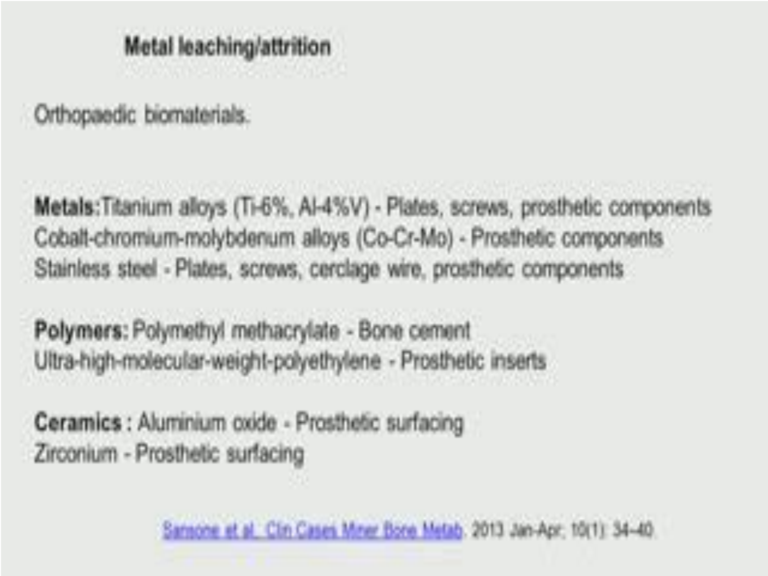

Then there is something called metal leaching metal attrition that is metal on metal joints there are joints there are metal and they start moving one on top of the other or one related to other is there is going to be attrition there could be metal leaching or sometimes is debris leaching, this is a big problem in orthopaedic biomaterials knee joints especially there because in orthopaedic they use metals titanium alloys which mainly used for plates screws prosthetic cobalt chromium molybdenum alloys for prosthetic stainless steel for plates screws wire polymers polymethyl methacrylate as a cementing agent ultra high molecular weight polyethylene as the prosthetic inserts ceramics aluminium oxide for prosthetic zirconium prosthetic surfacing. So, you could have metal leaching or metal debris even polymer debris are also possible, but more than polymer debris metal debris metal leaching causes more problems actually.

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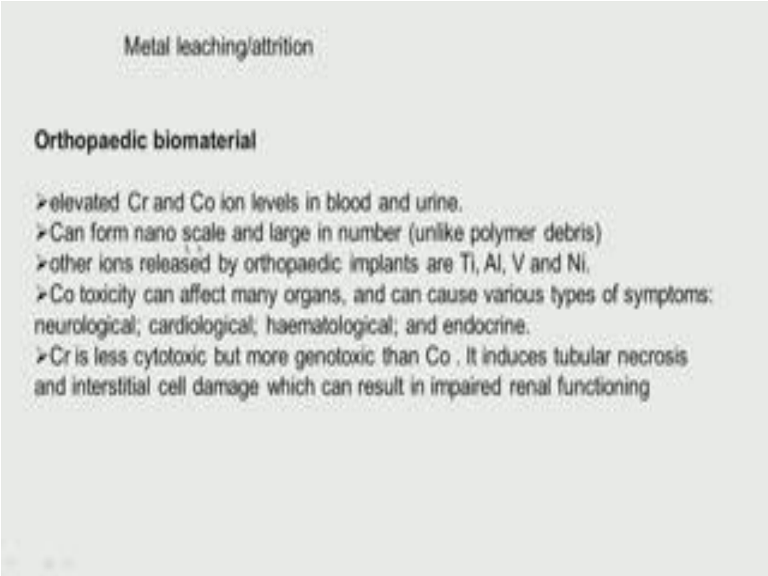

Because elevated chromium cobalt in blood and urine are observed in some cases they can even form non on a scale and large in number and like polymer other ions that are also released titanium aluminium vanadium nickel, but cobalt is the main chap that is a big problem in chromium cobalt toxicity can affect many organ organs neurological problem, cardiological problem, himatal hematological problem and endocrine problem.

Chromium is less cytotoxic than cobalt, but it also induces interstitial cell damage tubular necrosis which can affect your renal; that means, your kidneys. So, especially knee joints where people who had artificial metal knees always find leaching of this metal in the blood.

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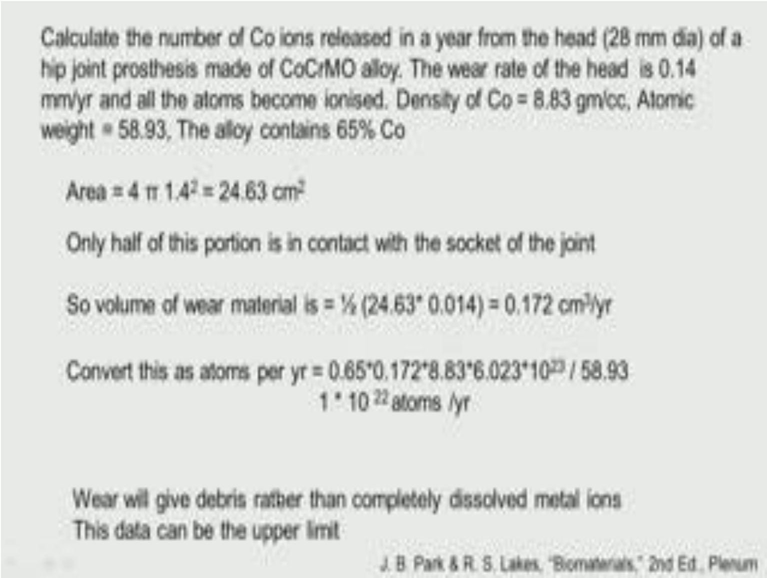

Let us look at a problem and this problem was taken from this reference, calculate the number of cobalt ions released from this cobalt chromium molybdenum, this contains 65 percentage cobalt of the head is 28 mm dia of a hip joint the very wear rate is 0.14 millimetre per year density of cobalt is 8.83, they want to find how many cobalt ions are released and so when it is released from the prosthesis only 65 percentage contains cobalt that is all is chromium and molybdenum.

So, let us look at the area because we said a head 28 mm 4 pi 1.4 square, now when you have you hip joint it is like a ball and socket it is only half of it is in contact with the socket the ball half of the ball is only in contact remaining half is outside. So, we will take only one half. So, we will divide this by one half. So, this is the area the volume is 1 half of 24.63 into 0.014 centimetre per year because this is the wear rate this is in millimetre. So, I divided I mean by 10.

So, many c c of cobalt, so, many c c of the alloy comes out of this only 65 percentage is cobalt. So, many c c of the alloy per year is coming out. So, what do we do we multiply by 0.65 because it is 65 percentage cobalt density of cobalt is 8.83 and then you know this is Avogadro number 6.023 10 power 23 divided by atomic weight is 58.93 here because we are converting that in to mole. So, that gives you 1 into 10 power 22 atoms of cobalt per year understand.

So, volume of the prosthetic is this much 65 percent is cobalt. So, we multiply by 0.65, now we are converting it into number of atoms. So, how do we convert it? So, how do we convert that we divide by 58.93 multiplied by Avogadro number also multiplied by the density of cobalt. So, 0.65 into 1 multiplied by 0.7; 0.172 is the c c of cobalt when we multiply by density of cobalt that will give you gram of cobalt that is 8.83 when we divide by 58.3 that molecular atomic weight of cobalt that will give you a mole of cobalt when we multiply by Avogadro number that will give the atoms of cobalt.

So, 10 power 22 atoms of cobalt are leaching out when there is aware of 0.14 of the hip joint, but of course, you are not going to have continuously cobalt purely dissolved there could be debris also small small bits and pieces, but this will be the upper limit, but there could be debris coming out not it will not be like a single; single ions of cobalt, but it is an very interesting problem.

So, many atoms of cobalt comes out per year and that based on the toxicity limits it could cost a certain cytotoxicity or systemic toxicity to the patient.

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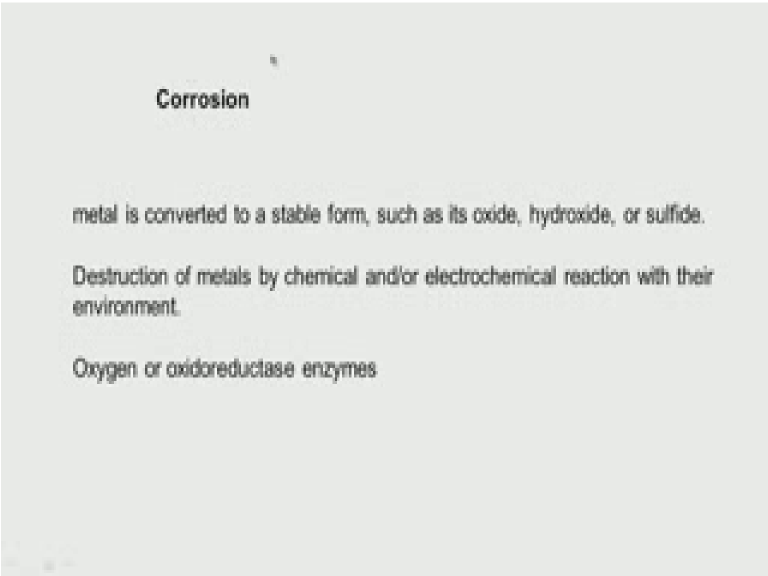

Corrosion that is a very big problem in metals corrosion and like polymers metals face this because of oxidation. So, the oxides of metals are form hydroxides of metals are formed sulphides of metals are formed. So, there could be chemical reaction there could be electric electrochemical reaction with their environment reaction because of oxygen because of the enzymes there are present in the body oxidoreductase. So, that they try to put in a oxygen in to the metal as you know our body fluids are very very corrosive you have dissolved oxygen we have enzymes we have salts because it contains chloride salts. So, all these are very corrosive and that leads to corrosion different types of corrosion we will look at.

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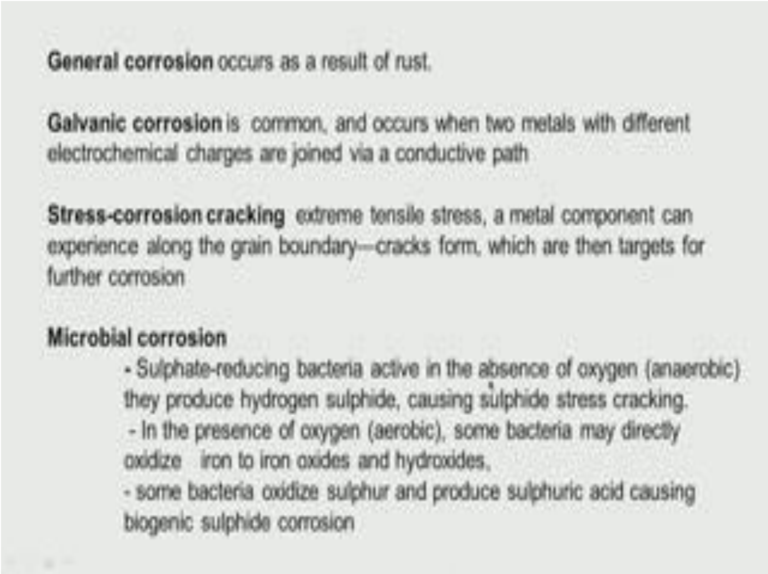

So, rust galvanic corrosion is a common and occurs when 2 metals with different electrochemical charges joined via a conductive path. So, if I have for example, even your prosthetic which contains cobalt molybdenum chromium. So, there could be galvanic type of because of electrochemical nature or if you have a certain biomaterial with 2 different metals one may act as an anode other may act as the cathode and there could be current and hence there could be corrosion. So, when we use dissimilar metals. In fact, we should avoid dissimilar metals and they were in contact that could be current flow which will lead to this galvanic corrosion.

So, the anode may start going down dissolving into the solution stress corrosion cracking extreme tensile stress especially when I am using along the grain boundary cracks could be forming or if I am having screws very tightly fitting there could be stress corrosion microbial corrosion because microbes we have sulphate reducing bacteria we have oxidoreductase all these can cause sulphate reducing bacteria activate the absence of oxygen generally anaerobic they produce hydrogen sulphide and cost sulphide stress cracking in the presence of oxygen aerobic bacteria will oxidize iron to iron oxides and hydroxides.

So, some bacteria oxidize sulphur to produce sulphuric acid which is again in acid which can lead to sulphide corrosion. So, all this can happen we can have an aerobic condition hydrogen sulphide is formed. So, sulphide stress cracking in the aerobic condition oxygen is there leading to oxides of iron hydroxides sulphur sometime is converted to sulphuric acid which leading to again biogenic sulphide corrosion. So, all these are possible because of microbes.

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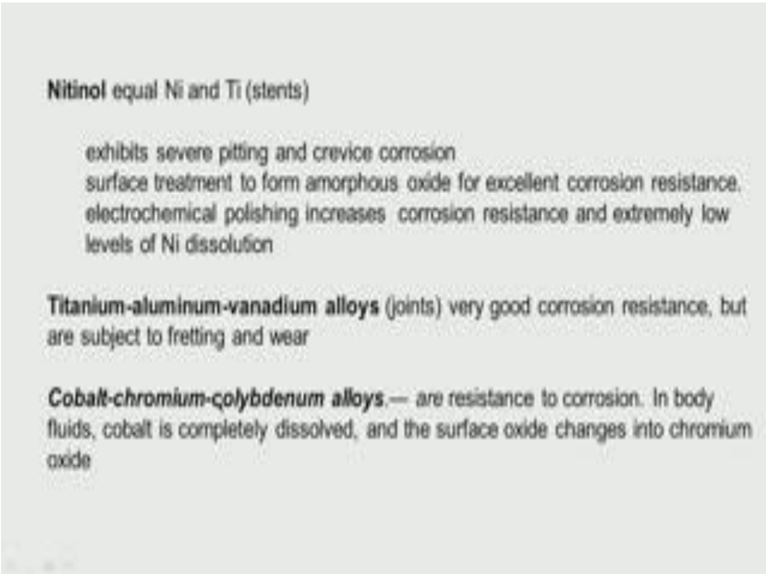

For example if we take a Nitinol it is a very popular material used in cardiovascular stands after an angiogram; angioplastic it is made up of nickel and titanium equal amounts it can exhibit severe pitting and crevice corrosion, but surface treatment to form amorphous oxide prevents the corrosion resistance. So, oxides can prevent corrosion resistance electrochemical polishing also increases corrosion resistance and it reduces the nickel dissolution. So, otherwise nickel maybe dissolving slowly now if you look at titanium aluminium vanadium alloys they are used in joints they are very good corrosion resistance, but are subject to fretting and wear because the aluminium can start wearing out cobalt chromium molybdenum sorry this mistake here molybdenum alloys are also resistance to corrosion.

In body fluids, but cobalt is a big problem it gets completely dissolved in the surface oxide changes into chromium oxide. So, cobalt release is a problem.

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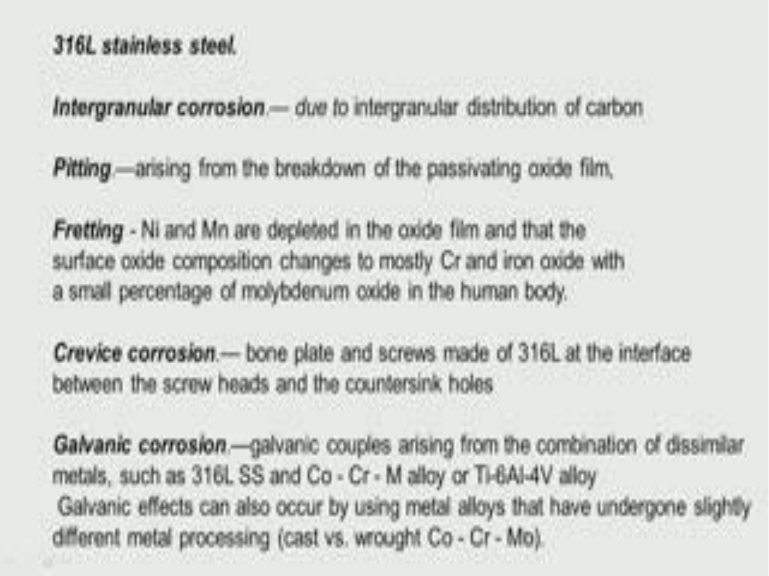

316L, it is cheap, it is very; it is very ubiquity as its used to quite a lot in orthopaedic, but then it can go into corrosion serious problem inter granular corrosion because carbon is also present and so, the heterogeneous carbon present can lead to corrosion pitting arising from the breakdown of the oxide layer. So, there could be pits formed as the oxides layers gets fretting nickel and manganese are depleted in the oxide film and the surface oxide composition changes mostly to a chromium and iron with a small percentage of molybdenum in the human body. So, these start going out that is called fretting crevice corrosion.

So, when you have a bone plate and screws made up of 316L at the interface the screw heads and the counter sink holes you can have this crevice corrosion.

Galvanic corrosion like as I mentioned if you have a metal dissimilar metals combination of 316L and cobalt chromium molybdenum or cobalt, chromium, titanium, aluminium, vanadium, alloys then you can have galvanic corrosion. So, 316 can have all sorts of corrosion. So, it is ideal material for only short duration and not for very long applications. So, you need to keep that in mind and galvanic corrosion can also occur by using metal alloys that have undergone slightly different metal processing cast versus wrought for example, if you take cobalt chromium molybdenum if you have 2 of these one made through casting another made through wrought then they can undergo galvanic corrosion.

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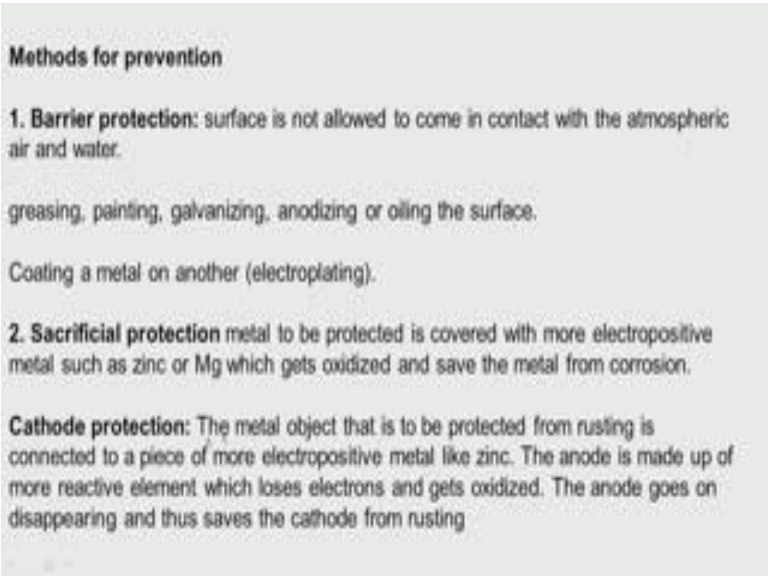

So, what are the methods barrier protection we can have a surface layer. So, that that layer prevents the metal from contact with atmosphere air water freezing painting galvanizing anodizing oiling the surface coating metal on another metal electroplating all these are barrier protection.

Another is sacrificial protection; that means you have another metal coating on the top like zinc or magnesium which gets oxidized. So, it prevents the main metal from getting corroded it is called sacrificial protection you sacrifice some other metal which gets oxidised third is cathode protection the metal object that is to be protected from rusting is connected to a metal of more electropositive metal like zinc the anode is made up of more reactive element which loses electrons and get oxidized. So, the anode goes on disappearing and saves the cathode from rusting. So, zinc could be the anode the metal which you want to protect could be the cathode. So, zinc will start going into solution and disappear for as the other material remains that is called the cathode protection. So, different ways of barrier protection are possible.

So, when there is a corrosion iron becomes iron oxide. So, what could be the molecular weight change sorry what could be the volume change?

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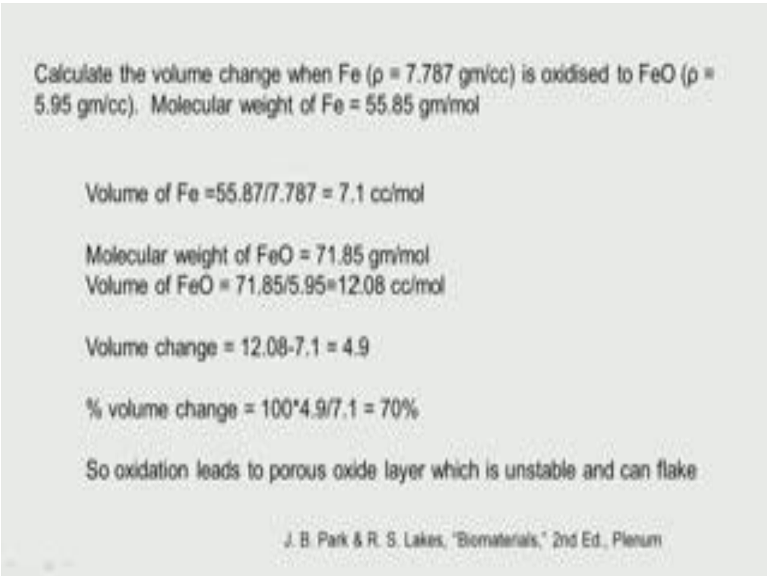

Calculate the volume change when iron of this density is oxidized to iron of this density. So, molecular weight of iron is this. So, it is quite simple volume of iron is 55.85 divided by 75 is this 7.1 c c per mole, molecular weight of iron oxide is 71.85; that means, iron plus oxygen 55.8 plus 16 that is 71. Volume of iron oxide is 71.85 divided by fine 5.95; 12.08 c c. So, we have the volume of iron we have the volume of iron oxide. So, look at this there is a big change in the volume therefore, the percentage volume change is 100

4.9 divided by original percentage change when iron gets iron oxide. So, when there is such a big change what happens this iron oxides becomes very unstable very loose it is like a flake you know it is very porous. So, it loses all the mechanical properties and like iron. So, that is a big problem you understand this problem.

So, iron density is 7.7 where as iron oxide density reduction in density obviously; that means, there will be increase in the volume that is about 70 percent increase in volume. So, how do you calculate? We use this density values and then used the molecular weight value. So, molecular weight of iron is 55.85, molecular weight of iron oxide is this plus another 16, 71.85. So, we take the molecular weight divided by the density to get c c and for both then the volume change 49. So, it has changed from 7.1 to 12.0. So, percentage is this difference divided by original into 100 percent that is a big change.

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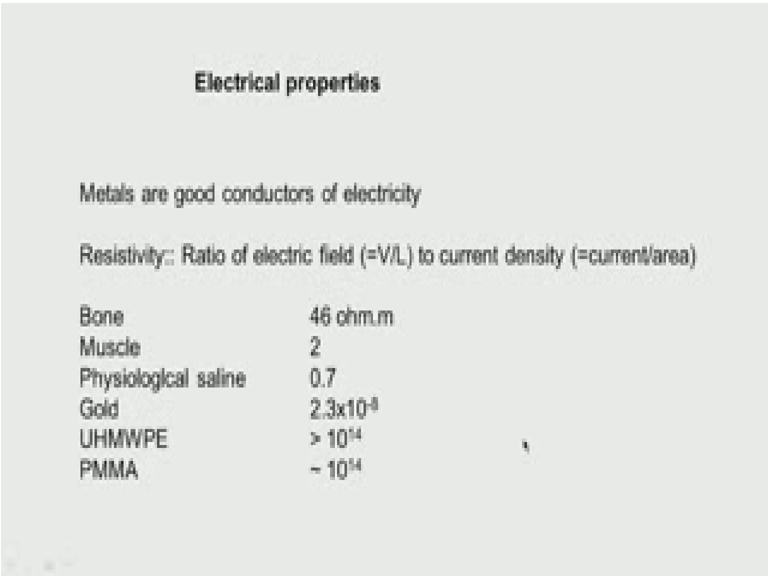

Now, let us look at electrical properties because electrochemical corrosion is a very serious problem in a biomaterials when we are using different types of materials joined together. So, we will look at it metals are good conductors of electricity. So, resistivity is the ratio of electric field to current density and if you look at bone resistivity is forty six ohms per metre sorry ohms meter muscle is 2 and gold is very very low ultra high molecular it is very very high when compared to these atoms actually.

So, and the polymers have very high resistivity and metals like gold have very lowest resistivity when compared to the various physiological body material.

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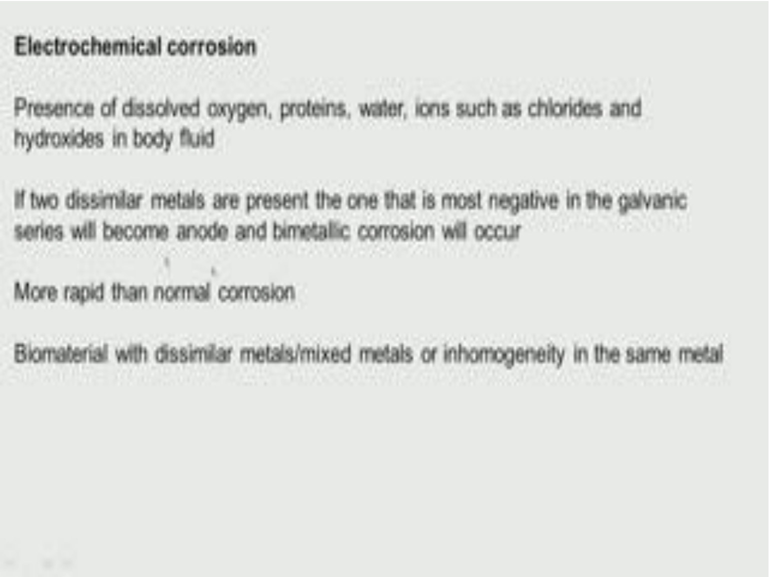

So, electrochemical corrosion I said presence of dissolved oxygen proteins water ions such as chlorides and hydroxides in the body fluid and if 2 dissimilar metals are present the one that is most negative in the galvanic series will become anode the other one becomes cathode what is this galvanic series we will look at it this corrosion is much more rapid than the normal. So, this happens biomaterials with dissimilar metals mixed metals or even inhomogeneity in the same material. So, if you have alloys cobalt chromium and so on inhomogeneity. So, one could be acting as anode other could be acting as cathode and there could be current flow and there could be galvanic corrosion.

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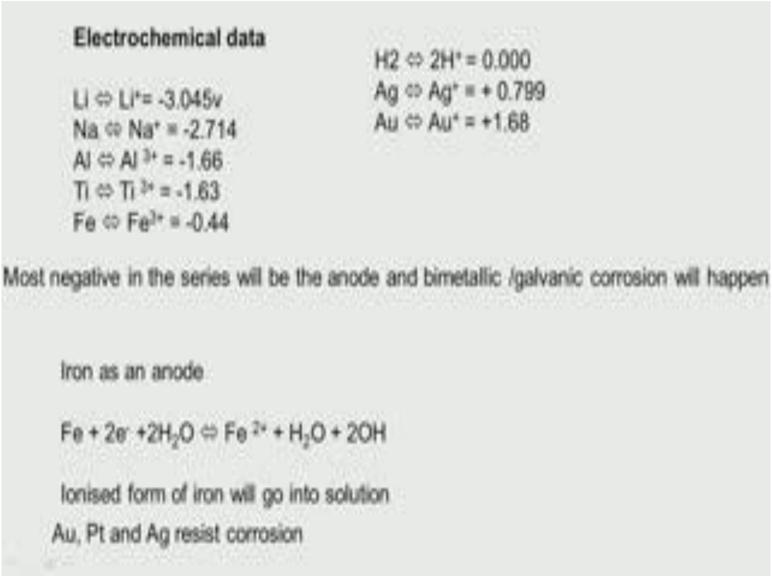

So, what is this most negative in the galvanic series, let us look at the galvanic series electrochemical data lithium going to lithium plus minus 3.05 volts sodium going to sodium plus minus 2.7 aluminium going to aluminium 3 plus minus 1.6 titanium going to titanium 3 plus minus 1.6 titanium going to titanium 3 plus minus 1.63 iron going to iron 3 plus minus 4 point hydrogen going to 2 H plus 0 silver going to silver plus 0.799 gold going to going gold plus 1.1; 1.68. So, most negative in the series will be the anode and other one will be cathode. So, there will be corrosion that is taking place and that particular material will be dissolving. So, if I have a iron and gold most negative. So, this will become anode. So, Fe 2 electrons can become Fe 2 plus. So, this can go into solution.

That is why these gold silver even platinum can resist corrosion that is why when you go into a biosensors lead wires they always use the noble metals. So, look at this. So, motion negative will be the anode. So, if I am having a aluminium and iron this will become the anode in this will become the cathode iron and gold, this will become the anode this will become the cathode and this is the reaction for iron plus 2 electron. So, you get Fe 2 plus. So, this starts going into solution. So, the electrochemical corrosion galvanic corrosion is much more serious problem and one is to keep in mind when designing biomaterial having dissimilar materials in contact with each other. So, you may have to have a ceramic or you may have to a insulator or a polymer in between. So, that the galvanic current is broken down.

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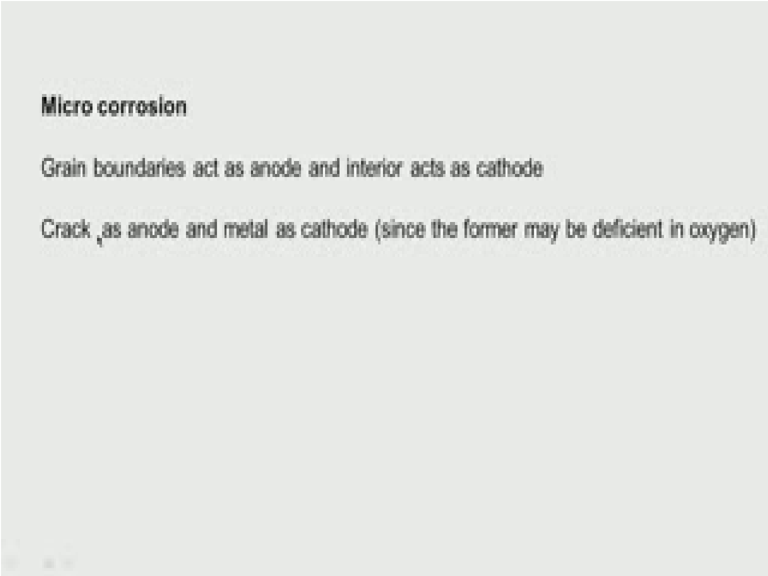

Of course as you can also have a micro corrosion because the grain boundaries act as anode and the interior part acts as the cathode. So, there could be a current flowing and grain boundaries could get disturbed sometimes cracks in metals can act as an anode and metal remaining metal can be a cathode because the cracks may have less or more of a oxygen. So, there is a difference inhomogeneity in the amount of oxygen present. So, that is called the micro corrosion that also could be a serious problem. So, metals have this particular issue of a normal corrosion because of presence of oxygen because of presence of aerobic bacteria, which oxidizes sulphur reducing bacteria in the anaerobic condition forms hydrogen sulphide, sulphide cracking or even formation of sulphuric acid so then the dissimilar metal type of corrosion. So, one is looking at using a fascinating layer looking at sacrificing sacrificial and materials and so on actually.

Thank you very much for your time.