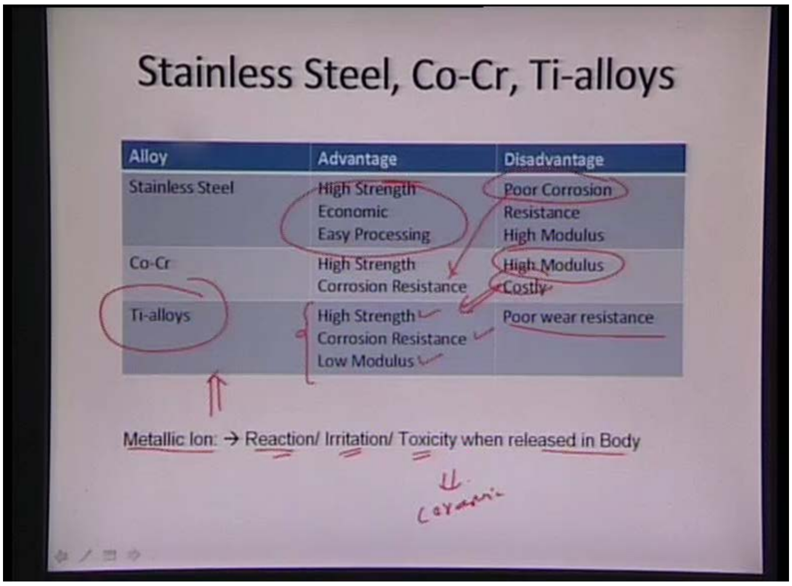
Introduction to Biomaterials

Prof. Bikramjit Basu
Prof. Kantesh Balani
Department of Materials and Metallurgical Engineering
Indian Institute of Technology, Kanpur

Module No. # 01
Lecture No. # 17
Co-Cr-Mo Alloys

In this lecture, we learnt about titanium alloys, titanium bio-metallic alloys and we have learnt already about stainless steel, cobalt, chromium alloys. So, in this lecture, we will learn something more about titanium alloys.

(Refer Slide Time: 00:27)



Stainless Steel, Co-Cr, Ti-alloys

Alloy	Advantage	Disadvantage
Stainless Steel	High Strength Economic Easy Processing	Poor Corrosion Resistance High Modulus
Co-Cr	High Strength Corrosion Resistance	High Modulus Costly
Ti-alloys	High Strength Corrosion Resistance Low Modulus	Poor wear resistance

Metallic Ion: → Reaction/ Irritation/ Toxicity when released in Body

⇓

Ceramic

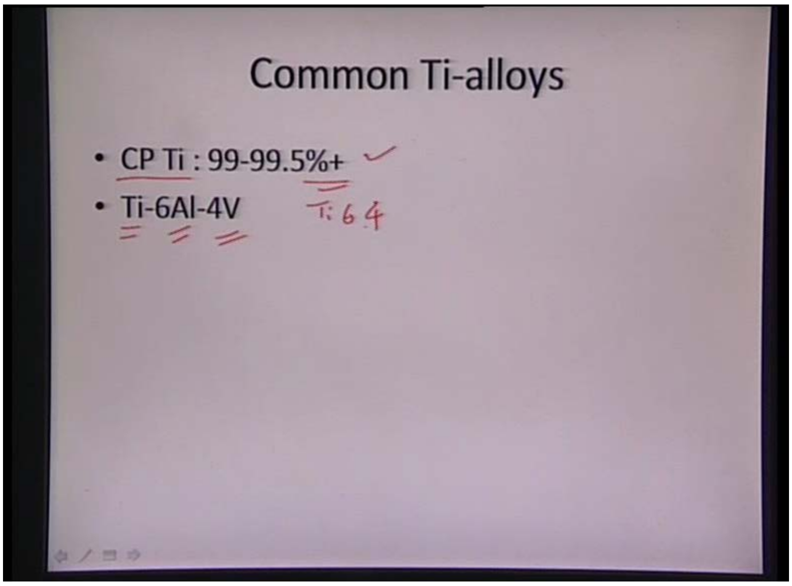
So, as we had realized earlier that stainless steel, it has a basically high strength, that is, economic. It has easy processing, but the problem mainly with the stainless steel was that it has very poor corrosion resistance. So, that is the reason we went on to the cobalt chromium alloys and there we realized that it has very good strength. It has high corrosion resistance, but the problem is, it is very costly and still it has very high modulus. So, if a material is a very high modulus, where essentially what happens that they start thinking it has, I do not need to be here and then, it will start getting reabsorbed into the body.

So, that is the reason we want to come back to a material which has little load lower modulus and that thing is been sufficed by titanium alloy. So, they provide a good combination of high strength, good corrosion resistance, low modulus, but the only problem with the titanium alloys is that they have very poor wear resistance. So, to counter act the poor wear resistance to generate titanium alloys, they need to be supplied with some sort of a surface coatings. So, surface coating, they take care of the wear parts. So, attend to enhance the surface wear resistance of the titanium implants.

At the same time, we can also apply some sort of a coating which is much more biocompatible in nature. So, then titanium alloy which is which has a very poor wear resistance and then we can also apply certain, some sort of a coating which can assist some bone integration on to its surface, so that coatings can be more of ceramic in nature, such as hydroxyapatite. Then, once the coating of hydroxyapatite based ceramic is applied, it is applied on to the titanium implant. Then, it can basically take care of the lower wear resistance of titanium and it can impart with superior wear properties.

Also, it can provide a base for service to grow and get adhere and proliferate on the implants surface and there is one more (( )) of titanium alloy Titanium 6 aluminum 4 vanadium. It has a metallic ion concentration and that basically can tend to react irritate or induce some toxicity when it is released into the body. So, in order to eliminate or to reduce the effects of this ion release into the body, again the sort of some ceramic coatings can also come for the rescue. Then, ceramic coatings that has a barrier and they do not allow the ions to flow easily from the implant surface to the surface of the material.

(Refer Slide Time: 02:43)



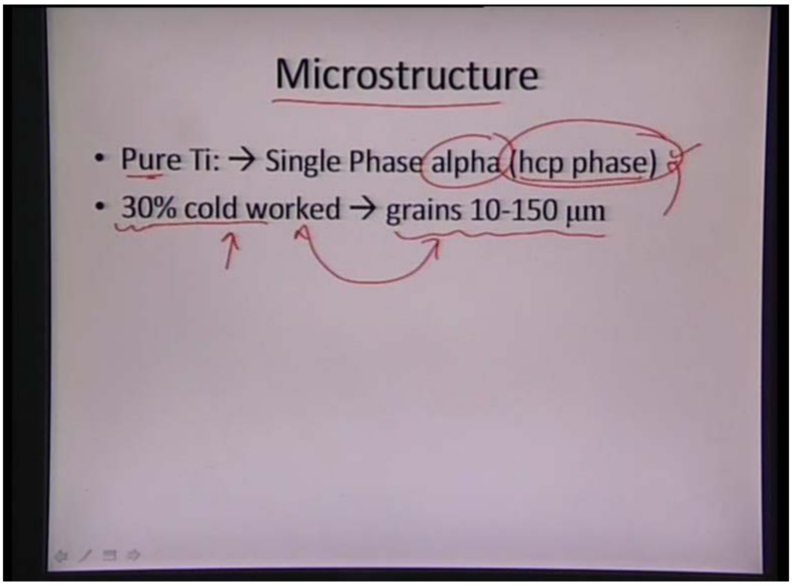
Common Ti-alloys

- CP Ti : 99-99.5%+
- Ti-6Al-4V

Ti 6 4

Commonly, the titanium alloys, they are the two common titanium alloys which are predominant in the medical industry or commercially pure titanium, which is approximately 89.9 percent to 99.5 percent plus purity. So, that is been widely utilized in the biomedical industry as well as there is a combination of titanium with 6 percent aluminum and 4 percent vanadium. So, this area is also called Ti-6Al-V, 6Al-4V. So, it is also called Ti-6-4 for easiness in the use but these are the two very commonly used titanium alloys and which are utilized in the biomedical industry.

(Refer Slide Time: 03:24)

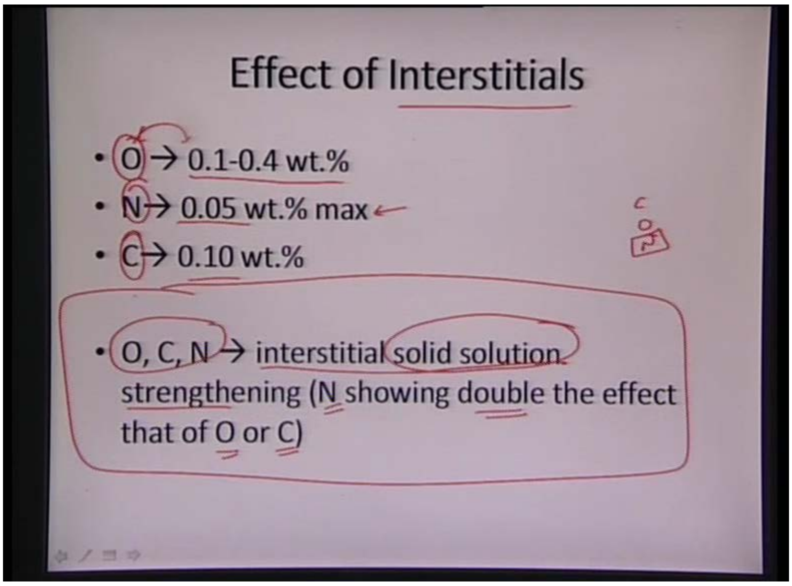


Microstructure

- Pure Ti: → Single Phase alpha (hcp phase)
- 30% cold worked → grains 10-150 μm

Coming to the microstructure part of it, the pure titanium, that is basically hexagon hcp phase and the phase is called alpha phase. So, pure titanium appears more, it is more of a single phase material and it is hcp and owning to the limited hcp slip place which are available in an hcp crystal, it has very limited process ability in terms of; it has very limited number of slip plays. So, that is generally very difficult to process as such. Again, this particular titanium alloy, this generally cold work to achieve grains in the order of 10 to 150 micrometers in size. So, ideally we can get a single phase structure titanium alloy and to basically induce much more strengthening, we go with the cold working part in the approximately 30 percent. Cold working is given to the titanium alloy in order to achieve grains which are to the order of 10 to 150 micrometers in diameter.

(Refer Slide Time: 04:19)



Effect of Interstitials

- O → 0.1-0.4 wt.%
- N → 0.05 wt.% max
- C → 0.10 wt.%

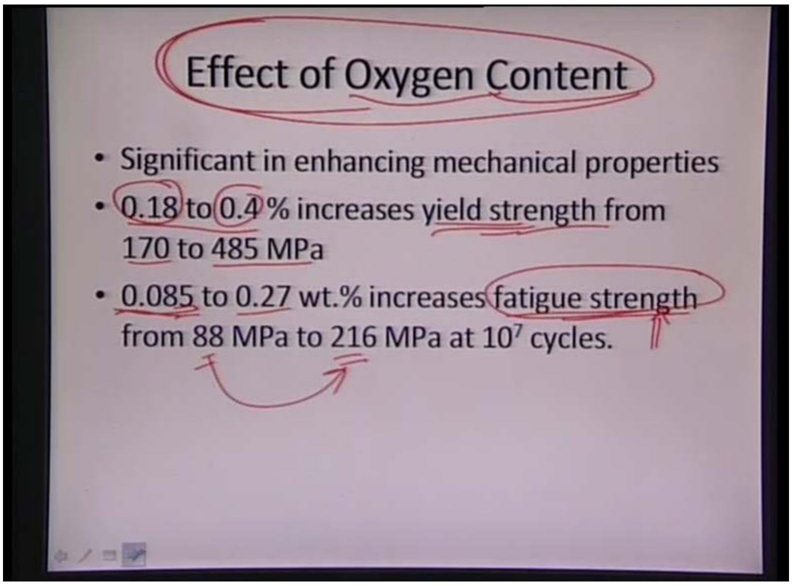
C
O
N

- O, C, N → interstitial solid solution strengthening (N showing double the effect that of O or C)

There can be addition of secondary interstitial into the titanium and those can be, oxygen, nitrogen or carbon. They go into the interstitial size of the titanium and from that, we can have a various combination. They are certain grades which basically differentiate the titanium alloy. They go from grade 1, grade 2, grade 3, grade 4 depending on the oxygen contained into the titanium alloy oxygen. It can be from 0.1 to 0.4 weight percent. Nitrogen can be approximately 0.05 weight percent maximum and carbon can be up to 0.10 weight percent into the titanium alloy, basically the function of all these interstitials, so that we can achieve interstitial solid solution strengthening. So, we can see that once the carbon or oxygen or nitrogen in the interstitial site, basically they induce solid solution strength, strengthening of the titanium alloy.

It is also been observed by researchers that nitrogen is showed at the approximated double the effect of either oxygen, that of oxygen or carbon. So, if we have nitrogen sitting in the interstitial, it will provide much more strengthening effect in comparison to that of our oxygen and carbon, but at the same time, we can add maximum nitrogen of around 0.05 weight percent. So, this is the overall effect of the interstitial, that oxygen, carbon and nitrogen, they just go and sit in the interstitial site and nitrogen shows approximately double effect of oxygen or carbon to provide strengthening of the solid solutions strengthening, interstitial solid solution strength.

(Refer Slide Time: 05:56)



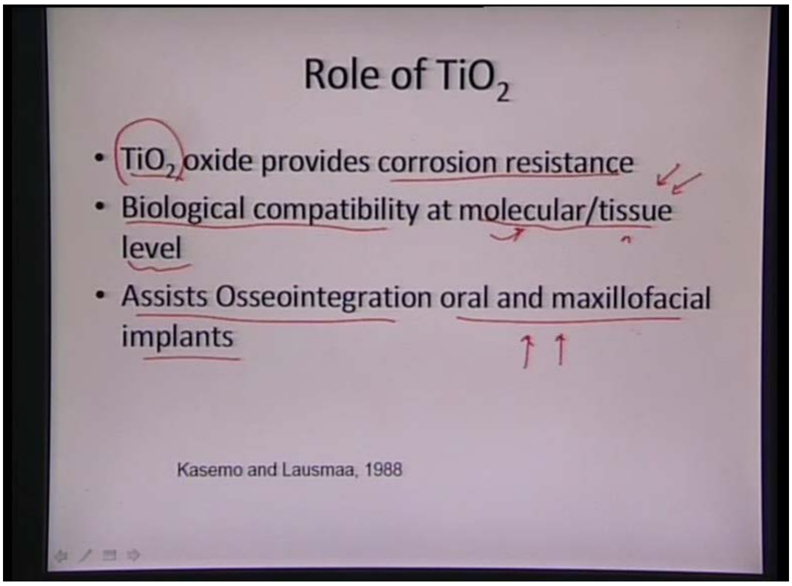
Effect of Oxygen Content

- Significant in enhancing mechanical properties
- 0.18 to 0.4 % increases yield strength from 170 to 485 MPa
- 0.085 to 0.27 wt.% increases fatigue strength from 88 MPa to 216 MPa at 10^7 cycles.

Oxygen is also very predominant in terms of in a single mechanical property, like if we increase the oxygen content from 0.18 to 0.4 percent, the yield strength will increase dramatically from 170 to 485 Mpa. So, approximately more than two and half times improvement, it can show in the yield strength which is by enhancing, by doubling the oxygen content. So, that is the approximate sort of dependence of oxygen content in the interstitial. So, once we have titanium, if we started inducing oxygen to a larger percentage, it will enhance the yield strength at the same time. If we increase the oxygen content from 0.085 to 0.27, then weight percent will also see an increase in the fatigue strength.

So, we see that fatigue strength is increasing approximately from 88 mpa to 216 mpa. So, it is also showing approximately, if we increase that oxygen content approximate to double or triple seen type of effect see in the fatigue strength as well. So, we can realize that the oxygen content is very useful in terms of higher, oxygen content is much useful in terms of increasing the yield strength, at the same time increasing the fatigue strength because those site act as some high energy regime and it becomes difficult for the slip to occur. That basically provides increase in the yield strength or the fatigue strength of the particular titanium alloy and a corrosion resistance comes in the titanium alloy because of the presence of this titanium oxide layer.

(Refer Slide Time: 07:26)



Role of TiO_2

- TiO_2 oxide provides corrosion resistance
- Biological compatibility at molecular/tissue level
- Assists Osseointegration oral and maxillofacial implants

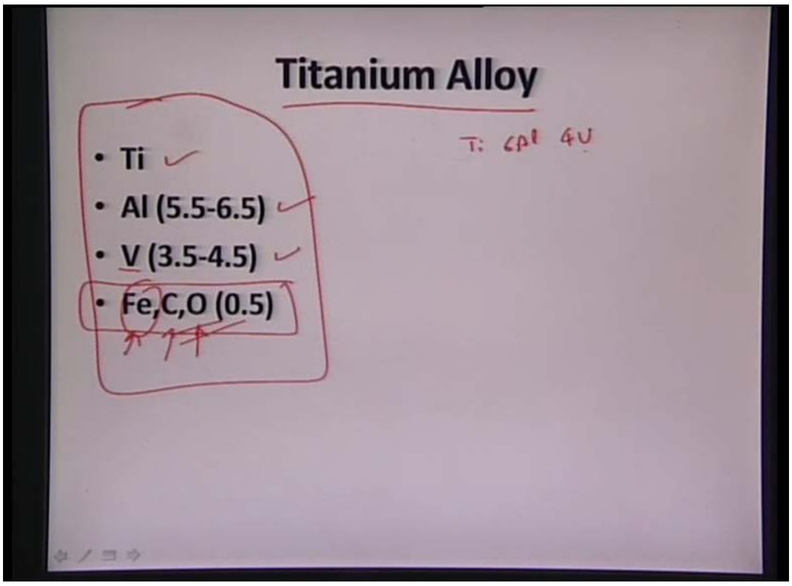
Kasemo and Lausmaa, 1988

So, titanium oxide layer provides as a barrier for the surface to interact the titanium implant and this titanium oxide, which is responsible for rendering the corrosion resistance to the titanium alloy. At the same time, TiO2 is found to be much more biologically compatible even at the molecular or tissue level because of its similarity. It can allow that cells or tissues to grow on its surface because you can see any toxic effect, so that biological compatibility is available even at molecular skill or even at the tissue level.

So, those tissues find a very friendly environment on the titanium oxide surface because it is no more titanium. Titanium is basically covered with the impervase layer of titanium oxide. So, there is no release of titanium ions through this particular titanium oxide and the titanium oxide is much more bio-friendly. It is very bio alert in nature and that does not induce some irritation or toxicity effect into the cells or tissues. So, cells and tissues find a very comfortable environment in terms of their adhesion, in terms of their growth, in terms of their proliferation. So, that is the advantage we achieve from the titanium oxide layer, that it to impact much corrosion resistance even in the very severe body fluid environments.

Again, it can also impact much biological compatibility, both at molecular level as well as the tissue level and also researchers have found Kasemo and Lausmaa, they also found that titanium oxide, it assists osseointegration, oral and maxillofacial implants. So, that is also the thing which has been observed by the titanium oxide, that is much more bio-friendly in nature. It allows osseointegration oral and also maxillofacial implants.

(Refer Slide Time: 09:13)



Titanium Alloy

Ti: 6Al 4V

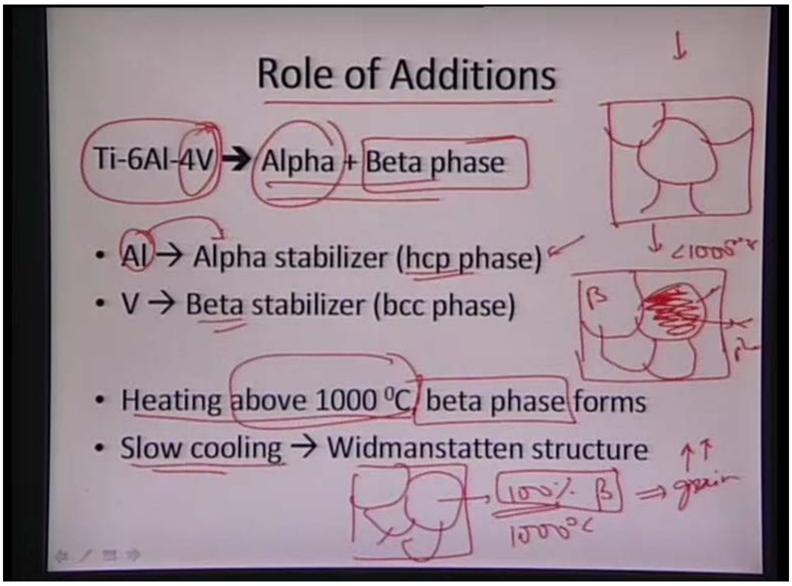
- Ti
- Al (5.5-6.5)
- V (3.5-4.5)
- Fe,C,O (0.5)

Coming to the titanium alloy, generally the titanium itself is not that stronger in nature. So, it also needs certain reinforcement because titanium is as a single phase material and if you start making it dual phase material, so instead of having only alpha at the hcp phase, if you start inducing the secondary phase, we can also get this strengthening from the secondary precipitate. Why? Because it will also impact the impediment to this location motion, it can also generate some new slip systems which can be available for the slip to occur. So, in that particular manner, it will enhance its ductility. So, the personal part is basically enhanced to the same time the strength part can also get enhanced because of the dual phase microstructure.

So, in the titanium alloy, we see we have base as titanium and generally, this is called titanium 6 aluminum and 4 vanadium. So, we generally see aluminum between 5.5 to 6.5 vanadium between 3.5 to 4.5 and we have set some secondary reinforcement as well. That can be iron, carbon, oxygen, and they also impart strengthening in terms of increasing either the yield strength or the fatigue strength.

so that part also can be achieved from the interstitial such as carbon and oxygen so and we can have also have some other reinforcements which can go from iron nickel and so on, but over all this titanium alloy, it is also called titanium 6 aluminum 4 vanadium. It is the very popular material as a biomedical implant material and it consists of aluminum around 6 percent and vanadium of around 4 percent and wastage around carbon oxygen and so on.

(Refer Slide time: 10:48)



Role of Additions

Ti-6Al-4V → Alpha + Beta phase

- Al → Alpha stabilizer (hcp phase)
- V → Beta stabilizer (bcc phase)

- Heating above 1000 °C, beta phase forms
- Slow cooling → Widmanstatten structure

Again, as I said earlier, the role of additions, they go out to titanium 6 aluminum and 4 vanadium, it forms a dual phase microstructure. So, alpha comes basically from the titanium part, at the same time alpha is also been stabilized by aluminum. So, aluminum also act as a alpha stabilizer. It renders making hcp phase much more stable, but the presence of vanadium helps in a forming a beta phase. So, we see this titanium 6 aluminium 4 vanadium, it is a combination of alpha plus beta phase.

So, now instead of having a single phase, like in case of titanium, we read only single phase which was nothing but only alpha. Along this case, we see that we have dual microstructure, so we are seeing kind of a dual microstructure out here and in this case, some sudden pockets are only beta. So, we can see this alpha plus beta. So, we see this is beta and this is again alpha. So, we see a dual phase microstructure, which basically assist as in terms of achieving even higher strengths and a very high fatigue strength once we have a dual phase microstructure, that is advantage with achieving using the secondary alloys, such as aluminum and vanadium to impart much more increase in the yield strength and the fatigue strength of titanium alloy in itself.

One more thing which happens with the titanium 6 aluminum 4 vanadium is that once we heated above 1000 degree centigrade, we will see the formation of beta phase because beta phase is stable at high temperature. So, once we go above 1000 degrees centigrade, we will see a microstructure which is full of beta. So, we will see 100 percent beta structure which forms once we heat this particular material above 1000 degree centigrade. Once you start cooling it very slowly, then what will happen that the materials basically we retained at very high temperature for a very long time and it cools on very slowly. So, this much more increases in the grain size, so that is the problem with the slower cooling.

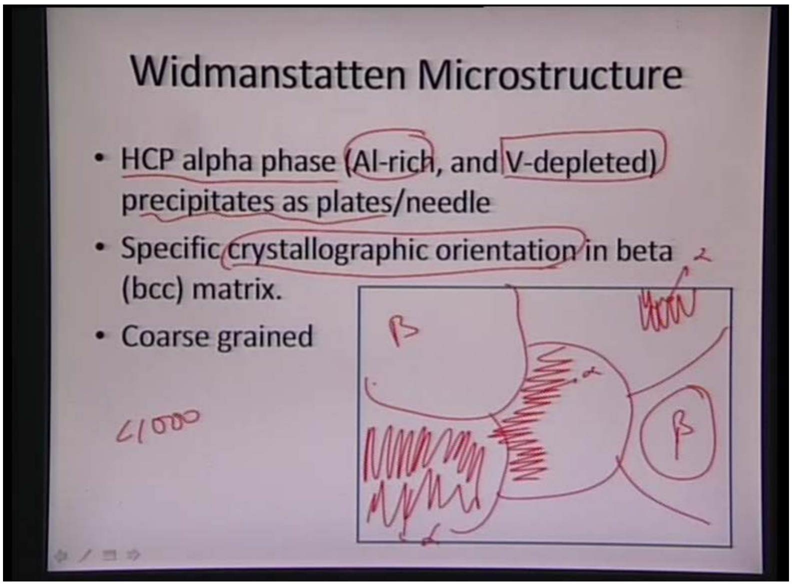
Let me tend to see something called Widmanstatten structure. So, in the Widmanstatten structure, you basically have structure like that. I will just draw it here that we see a structure in which initially, we will have only beta grace, once it is heated at high temperature. So, in this case, we have greater than 1000 degrees centigrade. We see completely 100 percent beta and as soon as we start cooling it down slowly, we will see that increase in the grain size. So, we will see, observe increase grain size and after certain temperature below 1000 degree centigrade, we will see the nucleation of alpha phase as well. So, in this particular case, we will see bigger beta grace, which were stable at more than 1000 degree centigrade and we see nucleation of alpha phase.

So, in this particular case, we have this larger beta grace and in that, we see a needle like secondary alpha phase and this structure is not that good. Why? Because it can be very highly brittle and this because it is a grain size is very huge and also it is more like a needle structure. So, needle, it means it can induce very high stress concentration factor. So, that is the reason this structure is not so preferable. So, we see very huge beta grace and in those, once we start cooling it very slowly to lesser than 1000 degrees centigrade, we see that the alpha grains which are hcp, they start precipitating. Since, it is a needle like structure, this structure can induce very high stress concentration factor near its step because it is a needle like structure, so that is the reason it can be very deleterious.

So, we will not achieve that sort of a strengthening or the toughening what we really expected to see in this particular material. So, that is the way, we need to modify somehow in terms of the heat treatment, so that we can achieve a structure which is much more compatible in terms of its mechanical properties. So, that is the, though it has certain advantages in terms of its additions, but this low cooling is inducing some deleterious effect in this particular material and a grain size, they can basically be more than even 500 microns. At this particular grain size, the properties mechanical properties will be very inferior because of the Hall phase relationships because our grain size to the order of around more than 500 macrons to the oral mechanical properties may be such as field strength, they will be very inferior.

So, that is the overall negativity, which can be induced just by processing itself because in this case, we are taking the material at very high temperature, more than 1000 degrees centigrade. We will attain beta to stabilize and then, we are allowing the alpha phase to form an equilibration. So, we are doing a very slow cooling and because of that, we see that the grain size have extended to a very huge extent, may be they have gone up to more than 500 microns. Then, this particular nucleation will cause hcp phase to form which is nothing, but alpha, which is again more like a needle like structure and that is in you see this negative effect.

(Refer Slide Time: 15:54)



Widmanstatten Microstructure

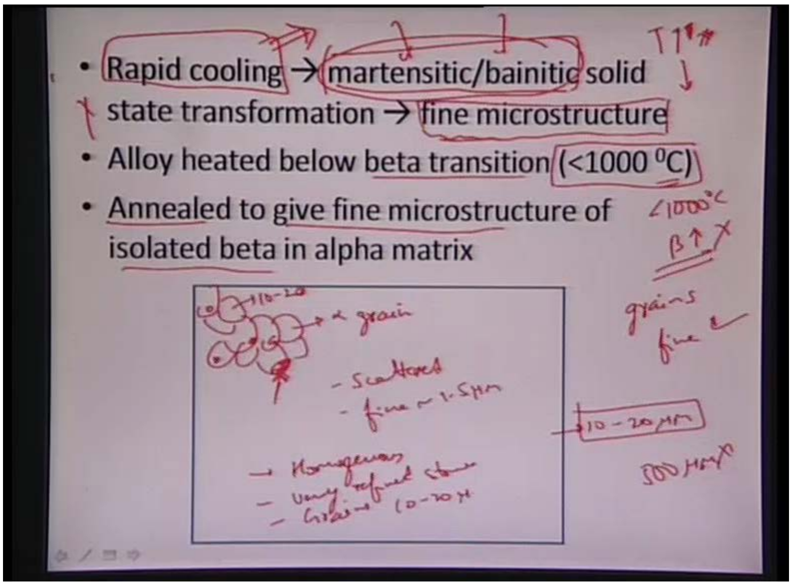
- HCP alpha phase (Al-rich, and V-depleted) precipitates as plates/needle
- Specific crystallographic orientation in beta (bcc) matrix.
- Coarse grained

So, we can see this Widmanstatten structure. It is basically, we see that the hcp alpha phase which is aluminum rich again, which is when depleted in the vanadium part, it starts precipitating as a plate or needle. So, we see that we had grace like this for the beta and then, in that we see the nucleation of this alpha phase, which can start nucleating at the within like this. Then, we have just beta phase and then, again we will see alpha phase nucleating because it is alpha phase. It will be much more stable at less than thousand degrees centigrade. We will see more of the grains which are forming alpha now.

So, we will have much more reasons, which is started forming alpha and then, the original beta regions which were present because we had taken the particular material above 1000 degree centigrade. So, this is the initial beta and then, we start seeing the formation of alpha structure which is much more like and that induces specific crystallographic orientation in beta. So, this alpha is forming by precipitating in particular crystallographic orientation, so that is the reason it comes more like a needle like structure and that is again forming within the beta grain. So, we have alpha getting precipitated in certain directions of the beta phase. So, that is what is being observed out here and it is again a coarse grained material because the material has sting for the whole heat treatments for couple of arts.

So, that is what the problem with this particular material is. We are taken it to very high temperature, we are letting it be there for much time and then, we are doing a very slow cooling. That is the reason, the material undergoes a higher thermal exposure for a very long time and that is the reason, the grains remain very coarse. Again in that, we see that the alpha is getting precipitated in the bcc type beta matrix along certain crystallographic orientations. That is the reason; it appears more like a needle like structure and again this needle like structure can create very high stress concentration effects near its needle, along the needle edges and that is the reason, it is very old structure.

(Refer Slide Time: 18:03)



- Rapid cooling → martensitic/bainitic solid state transformation → fine microstructure
- Alloy heated below beta transition (<1000 ⁰C)
- Annealed to give fine microstructure of isolated beta in alpha matrix

So, to avoid that particular part, what can be done? We can do a rapid cooling and rapid cooling basically induces martensitic or bainitic type solid state transformation. Since, we have very rapid cooling; we can also achieve very fine microstructure. So, that is the advantage with this rapid cooling is that instead of, now very coarse Widmanstatten structure, we are seeing a martensitic or the bainitic type solid state transformation. At the same time, we are able to achieve very fine microstructure. So, we are not staying at the high temperature regime for a very long time, so temperature is not high any more. We are doing a very rapid cooling, so we go to the alloy excess of 1000 degree centigrade, but we cool the material very rapidly and that rapid cooling induces martensitic or bainitic type solid state transformation.

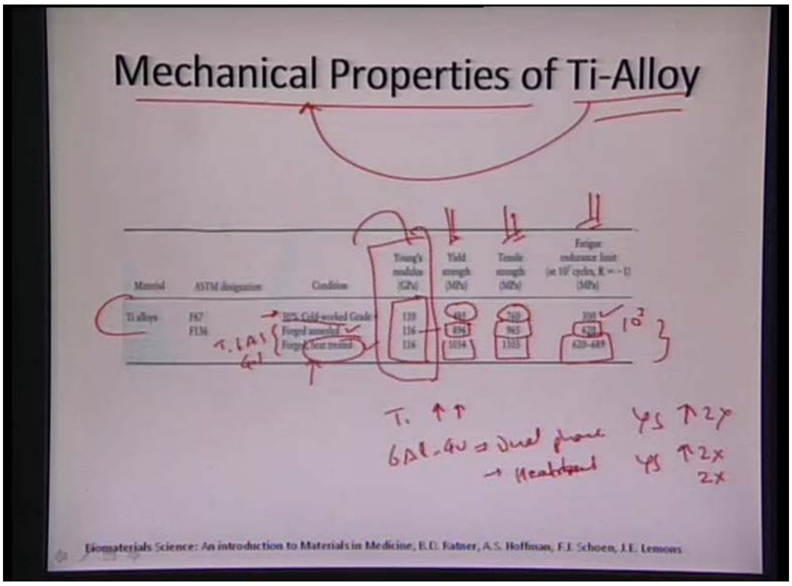
I will again, rapid cooling also induces very fine microstructure and again, the alloy is heated or cooled below the beta transition. So, we are not letting this particular material go above 1000 degrees centigrade. So, we are letting this condition happen below 1000 degrees centigrade. So, we are heating the material to lesser than 1000 degrees centigrade. So, we do not allow the beta to form completely. So, once beta is not formed completely, rapid cooling can induce martensitic or bainitic type transformation and at the same time, we are not allowing those grains to get coarser. So, grains remain fine and they are retained as such. So, we are not letting the grains get coarse because we are basically heating them much below 1000 degrees centigrade and then, they are basically annealed to give a very fine microstructure. In this particular case, we have isolated beta in alpha matrix, so that is what is happening now. We are not letting the beta form to a large extent.

So, we see very fine grains which can form and these fine grains, they to the order of round 10 to 20 microns. So, instead of going up more than 500 microns, there are no more 500 micrometers in diameter. They remain then the 10 to 20 micrometers regime and once we have this fine alpha regime, so we have alpha grains and we see that the beta is forming within it. So, we will see some beta is forming here and there, but it is again scattered. It is again very fine. Fine. It means, it is to the order of maybe, say 1 to 5 microns or so. This alpha is very fine because the grains themselves are around 10 to 20 micrometers. So, the beta which is basically getting nucleated at high temperature is again very fine and it is scattered throughout.

So, we see very homogeneous structure. Homogeneous again, very fine or very refined structure and grains are to the order of 10 to 20 micrometers in diameter. So, these are the certain advantages what we are getting from here that we are letting the material heat, but not above 1000 degrees centigrade. We keep the material lower than 1000 degrees centigrade and then, we do annealing or rapid cooling. Rapid cooling is basically returning those of alpha grains and we see some precipitation of the beta grains within the alpha grain.

So, we have alpha grains now in the order of 10 to 20 micrometers and then, beta is being precipitated here and there. Again, the size of beta precipitate is again couple of microns. So, over all what we get is very uniform structure, a very nicely dispersed beta in the alpha matrix. Now, we do not have any segregation of Widmanstatten structure anymore and the grains themselves have now limited size around 10 to 20 micrometers. So, over all properties, they grow multiple because of absence of this negative structures, such as the Widmanstatten structure or the coarse grain. So, the fine grain materials are now induced this Hall phase relationship and because of Hall phase relationship, we can get much superior properties, mechanical properties out which are stated in the earlier lecture. That is all, but one thing is basically seen is that titanium alloys, the young's modulus do not change much, even with certain additions.

(Refer Slide Time: 22:06)



Mechanical Properties of Ti-Alloy

Material	ASTM designation	Condition	Young's modulus (GPa)	Yield strength (MPa)	Tensile strength (MPa)	Fatigue endurance limit (at 10^7 cycles, R = −1) (MPa)
Ti alloys	F67	30% Cold-worked Grade	110	485	760	300
	F136	Forged annealed	116	896	965	620
		Forged, heat treated	116	1034	1103	620–689

Ti 6Al 4V

10^7

T. ↑↑

6Al-4V = Dual phase

→ Heattreat

YS ↑2×

YS ↑2×

2×

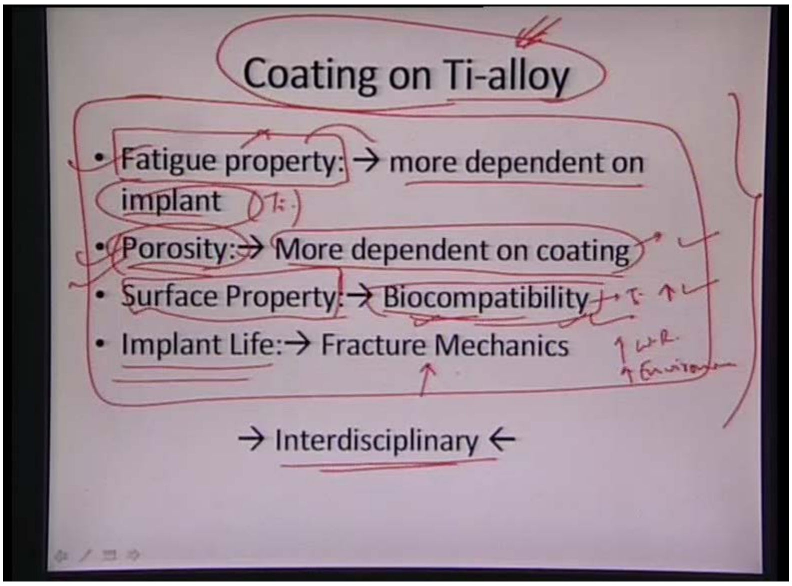
Biomaterials Science: An introduction to Materials in Medicine, B.D. Ratner, A.S. Hoffman, F.J. Schoen, J.E. Lemons

For commercially pure titanium, which is told to be 30 percent, we see yield strength which is to the order of around 485 tensile strength of around 76 mpa. It has fatigues address limit of around 300, but as far as we start adding certain alloys to it, like in case of titanium 6 aluminum 4 vanadium and that is that material is forced annealed and heat treated. So, we can see that one side is annealed.

We can see increase in the yield strength of 900 megapascals, tensile strength of around 1000 mpa and fatigues in this almost doubled. So, at the 10 power 7 cycles, again controlled heat treating can increase its yield strength to around 1034 megapascals, which is a more than a gigapascal. Tensile strength is also increased by certain extent around 1.1 gigapascal and fatigue strength is also increased to a certain extent. So, we can see how the role of heat treatment can be utilized in particular processing of titanium mullite to achieve enhanced mechanical properties. That is what it is like titanium alloy.

We are seeing certain properties. Once we add 6 aluminum four vanadium, we see a dual phase microstructure and the dual phase microstructure is basically assisting in the increase of yield strength, which is almost two times. Then, again heat treatment, control heat treatment can again increase yield strength by that matter of time and again, the fatigue entrance limit can also be increased by around two times. So, that is the way in which we can manipulate the properties of titanium alloy via certain secondly additions and as well as, performance of heat treatment in by utilizing heat treatment of the titanium alloy. So, those are the advantages of utilizing titanium alloy and performing the heat treatment because we can achieve very superior yield strength and tensile strength in the fatigue strength, though the Young’s modulus remaining same. Approximately, it is stimulated. It is not changed much, but the enhancement in the yield strength, tensile strength and fatigue strength is just phenomenal.

(Refer Slide Time: 24:20)



Coating on Ti-alloy

- Fatigue property: → more dependent on implant (Ti)
- Porosity: → More dependent on coating
- Surface Property: → Biocompatibility → Ti ↑
- Implant Life: → Fracture Mechanics

↑ W.R.
↑ Environment

→ Interdisciplinary ←

Again, titanium alloy as we learnt earlier, the titanium alloy it has a very poor wear resistance. At the same time, if we want to have very high superior fatigue property, it is basically more of the implant which takes the load and undergoes much more wear and tear in terms of taking the impact, in terms of taking the fatigue because ceramics is very brittle in nature. So, they cannot take much of the load or the fatigue. They do not have good fatigue property because they are ceramics, so they do not have enough yielding which can happen in the material. So, we see that the fatigue property is not much more dependent on the titanium alloy. So, that part we can see that fatigue property is more dependent on the implant or the titanium alloy, which forms the implant and to improve the fatigue property, it is only titanium alloy which is being responsible out here.

So, we need to perform certain heat treatments as we saw earlier, that we need to perform control heat treatment to take the material below 1000 degree centigrade and do the heat treatment. So, the yield strength and the fatigue strength, they increase to a large extent in comparison to the titanium itself. So, if you are utilizing commercially pure titanium, it might of fatigue strength, overall megapascals at 10 to the power 7 cycles, but if you take a titanium alloy and properly heated, it can have up to 600-700 mpa for same life cycle.

So, that identity essentially tells us that we have to utilize superior made of titanium if we want to achieve a very high or the enhanced fatigue properties and because that is mostly dependent on the implant because implant is the one, which is to take the overall load. Secondly, there is one more term called porosity and it is more dependent on the coating part because porosity, this essentially allows us to select what is the manner in which the surrounding environment of the body will interact with the implant material.

For a coating itself is bad, if coating is not good, not adherent to the cells, cell may not tend to adhere on the implant and will see a failure or there would not be any bounding between the bone and the surrounding tissues in the implant, in the surrounding tissues. So, that is the problem with the coating part that coating also is being mostly decided by the porosity part. We need to have enough porosity that cells can come and they can adhere onto the surface and they can clean themselves on those porosity, which is available to them and then form a strong bond with the bone implant.

So, that is one more criteria that we need to have a good porosity, which is similar to the size of the cells and that can provide anchoring to the cells. I will again, this surface coating is highly responsible in terms of the biocompatibility whose surface is the one which comes in direct contact with the cells. So, the surface itself is not biocompatible. We will see some toxic effects. Cells may not tend to adhere to the surface, cells may not proliferate and cells may not grow at all in the surface. So, we see that surface property is highly essential in terms of dictate in the cytocompatibility or the biocompatibility of the particular material.

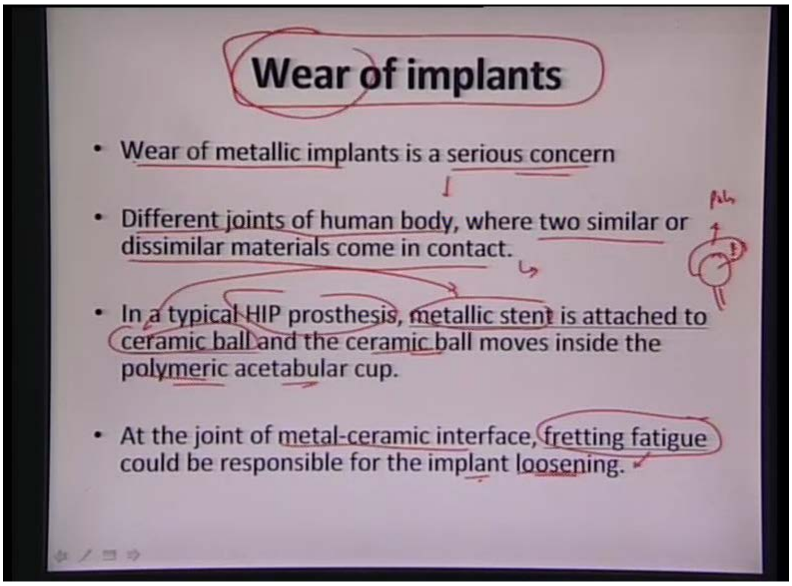
So, the secondary coating can be applied on the titanium alloy to render it much more, make it much more biocompatible. I will again, the implant life itself, it depends on many aspects, such as, it can depend on fatigue property, it can depend on the porosity and it can depend on the biocompatibility. Again, all these aspects are multidisciplinary in nature. The metallurgies will come and find out about the material, mechanical eligible come out and they will talk about, much more about the fatigue property. Then, a biologist will come, they will talk about the biocompatibility and a surgeon will come and talk about the overall applicability as an implant.

So, there are certain aspects to the titanium alloy which makes it complete, implant which can be inserted into the body. So, these coatings on the titanium alloy, they also are one of the essential components because they take care of porosity. They decide about the surface property also. They take care about whether cell will be much more compatible or not. They can also know some sort of porosity under the material. They can enhance the wear resistance of the material. So, they have to be the one's which much more the direct environment seems.

So, the coatings are one of the very essential components of the implant as such. So, this overall study of making a particular alloy as an implant, it is interdisciplinary in nature. So, that is what the underlining part that all these aspects should be taken or considered at once, so that we can find out the viability of using a particular material as a body implant. So, it is highly interdisciplinary in nature because we can see various aspects of this titanium implant or basically, being considered one can be fatigue property or the yield strength, which will decide the overall life of the fatigue. One material can withstand coming to it is biocompatibility part that whether the material itself is biocompatible or not. So, we need to implant certain coating to it, seeing about the wear resistance to it, seeing about the corrosion resistance. Again, we need some sort of coating which can we applied on to this particular material.

Then, coming on to the compatibility part of whether it is viable in terms of, either the cells can really (()) on to it or not or seeing about its biocompatibility and seeing about the mechanical property, whether its fracture will occur prolonged or it will come very shortly. So, those all parts make this particular study of interdisciplinary in nature and that is what makes it much more complicated.

(Refer slide Time: 29:54)



Wear of implants

- Wear of metallic implants is a serious concern
- Different joints of human body, where two similar or dissimilar materials come in contact.
- In a typical HIP prosthesis, metallic stent is attached to ceramic ball and the ceramic ball moves inside the polymeric acetabular cup.
- At the joint of metal-ceramic interface, fretting fatigue could be responsible for the implant loosening.

Now, coming to the wear of implants, so seeing all that part that it is materialist in nature, so wear is also one of the very essential components of designing an implant because any two joints which are lying nearby, they will tend to wear out with time. So, there is some movement between the two. Obviously, the material will undergo some sort of a wear, like we have acetabular cup and we have a ball and socket joint. So, in that we can see overlay between metallic surface and a polymeric or a ceramic surface.

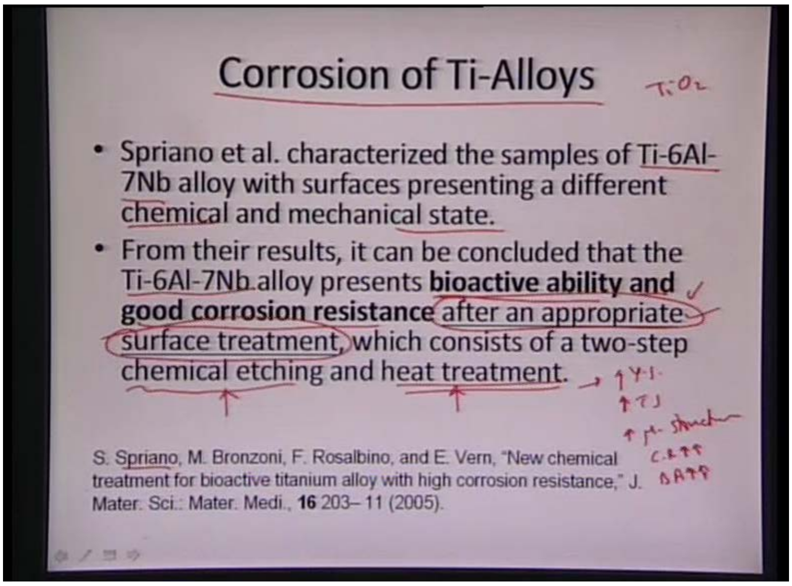
So, once we have to dissimilar metals which are being closer to one and another, we see they will be definitely; there will be some wear on to the particular or particular interphase. So, again wear of metallic implants is one of the very serious concerns because once it starts releasing some debri on to, while it is getting abraded or getting worn out, so those ions will start getting released into the body. Again, this wear will occur at the different joints of the human body and once, it is being implanted, once it is into the body, this have hardly any control.

So, all those debris which are being generated, that was trying to accumulate somewhere. So, those are being just released into the blood and that is we do not have any control after that. So, we need to have a material which will have a very superior wear resistance, once it is being implanted into the body. So, we need to see that wherever two similar or dissimilar metals of coming in contact, we design it so nicely that we can reduce either the corrosion resistance or we can increase the corrosion resistance or we can reduce the wear resistance or we enhance the wear resistance of those particular implants, like in case of a typical hip prosthesis. We see that a metallic stent is now attached to a ceramic ball.

So, because of the interphase between the ceramic ball and a metallic strength, there is some relative movement between the ceramic balls. I will again, it is moving either in the polymeric acetabular cup or we can see that a ball is made up of some material as stainless steel or something or it can be titanium implant. Then, over that we have a kind of a polymeric liner or a ceramic liner. Basically, between the metallic and ceramic interphase we can see much more of fretting wear, so that fretting wear can easily be causing some loosening of the implant.

So, what we see if we see that there is some wear is happening between the interphase between metal and ceramic interphase? That will tend to increase the gap between the two. So, once we see there is some debri which is being released or there is some gap which is being generated, obviously it will lead to the loosening of the implant and will lead a resurgery to insert that the implant back into the body and basically, do one more surgery. So, that particular material has failed because of poor wear resistance. So, that is highly essential part, highly critical part in terms of increasing its mechanical property and improving its wear resistance and coming back to one more important property of this titanium alloys about, it is corrosion resistance.

(Refer Slide Time: 32:50)



Corrosion of Ti-Alloys

TiO_2

- Spriano et al. characterized the samples of Ti-6Al-7Nb alloy with surfaces presenting a different chemical and mechanical state.
- From their results, it can be concluded that the Ti-6Al-7Nb alloy presents **bioactive ability and good corrosion resistance** after an appropriate surface treatment, which consists of a two-step chemical etching and heat treatment. → ↑ Y.S.

↑ T.S

↑ μ- structure

C.R ↑↑

BA ↑↑

S. Spriano, M. Bronzoni, F. Rosalbino, and E. Vern, "New chemical treatment for bioactive titanium alloy with high corrosion resistance," J. Mater. Sci.: Mater. Medi., **16** 203– 11 (2005).

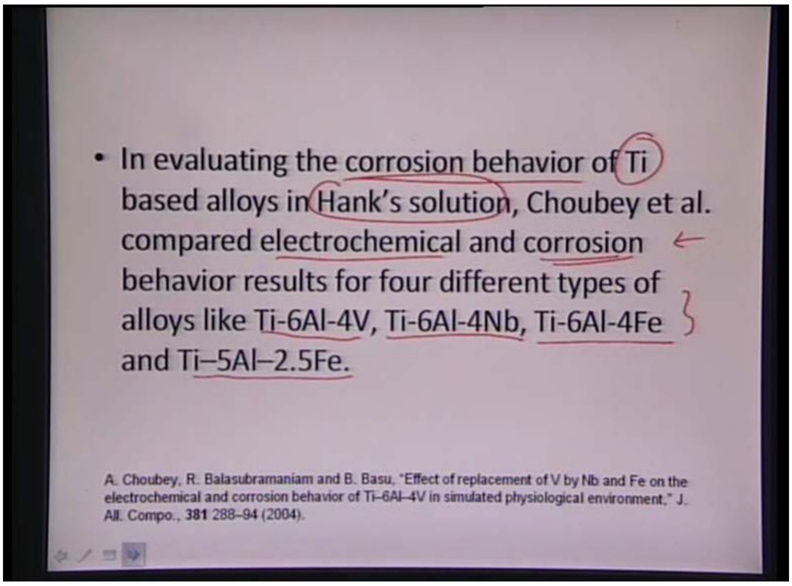
So, corrosion of titanium alloys is also one of the very critical parts because generally, we utilize a titanium alloy, which generally tend to be good corrosion resistance because of the formation of TiO_2 layer on its surface. So, there is a group Spriano which have characterized sample of titanium 6 aluminum 7 niobium alloys and with surfaces which were presented towards different chemical and mechanical states and from that, they have found that titanium 6 aluminum 7 niobium, it presents the bioactive ability and good corrosion resistance only after a appropriate surface treatment.

So, only when surface treatment is so nicely given to it in terms of having improved corrosion resistance, in terms of having a good biocompatible surface, in terms of having enough porosity on a surface, in terms of utilizing proper wear resistance corrosion resistance, at the same time, have it much more biocompatibility. So, that it can take the overall aspect of its compatibility with an implant and so, it basically consists of two steps. First of all is chemical etching and then, a heat treatment.

So, it needs to have some sort of a chemical treatment as well plus some heat treatment, so that it can attain superior yield strength, superior tensile strength. At the same time, it can achieve a good microstructure, so that the overall corrosion resistance is improved and overall bioactivity is also improved. So, that is what the overall study, which was carried out by the Spriano only after the appropriate surface treatment is given. Why? Because surface treatment is so important, surface is a one which will come and contact with the material.

So, once an implant is inserted into the body, it is only the surface which comes in direct contact with the material. So, it needs to be very compatible with the surrounding in terms of imparting a good corrosion resistance, in terms of let in the cells stick on to itself. Let in the cells grow on itself and proliferate to form certain networks with itself. So, that is what the overall study which was carried out by the Spriano.

(Refer Slide time: 35:09)



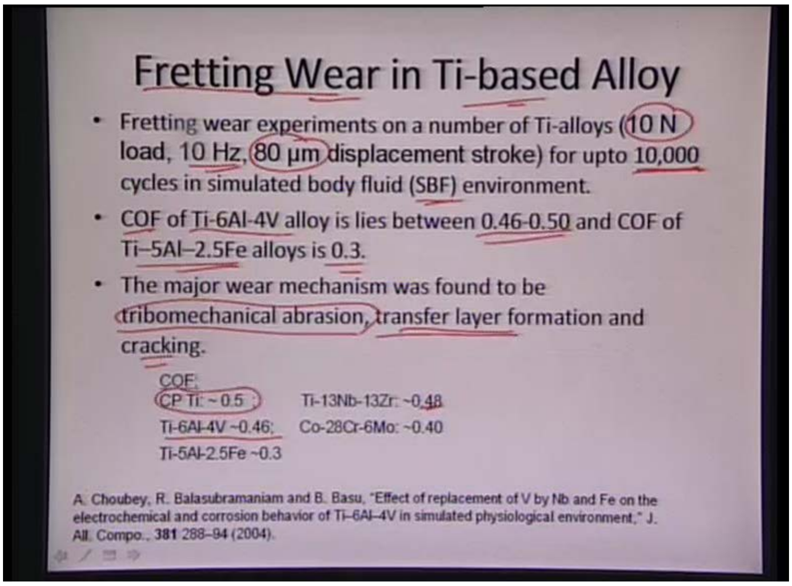
- In evaluating the corrosion behavior of Ti based alloys in Hank's solution, Choubey et al. compared electrochemical and corrosion behavior results for four different types of alloys like Ti-6Al-4V, Ti-6Al-4Nb, Ti-6Al-4Fe and Ti–5Al–2.5Fe.

A. Choubey, R. Balasubramaniam and B. Basu, "Effect of replacement of V by Nb and Fe on the electrochemical and corrosion behavior of Ti–6Al–4V in simulated physiological environment," J. All. Compo., **381** 288–94 (2004).

There is one more group of Choubey, which have utilized founding the corrosion behavior of titanium based alloys. So, there taken couple of alloys, this is titanium 6 aluminum 6 aluminum 4 vanadium, titanium 6 aluminum 4 niobium, titanium 6 aluminum 4 Fe, titanium 5 aluminum 2.5 Fe.

So, they have taken couple of four different types of alloys and they basically found, it is behavior in the Hank's solution. So, then they have compared what is the electrochemical and that corrosion behavior of all these alloys for different conditions, so that is what they have found out and at the same time, they also have done fretting wear of the titanium based alloys.

(Refer Slide Time: 35:41)



Fretting Wear in Ti-based Alloy

- Fretting wear experiments on a number of Ti-alloys (10 N load, 10 Hz, 80 μm displacement stroke) for upto 10,000 cycles in simulated body fluid (SBF) environment.
- COF of Ti-6Al-4V alloy is lies between 0.46-0.50 and COF of Ti–5Al–2.5Fe alloys is 0.3.
- The major wear mechanism was found to be tribomechanical abrasion, transfer layer formation and cracking.

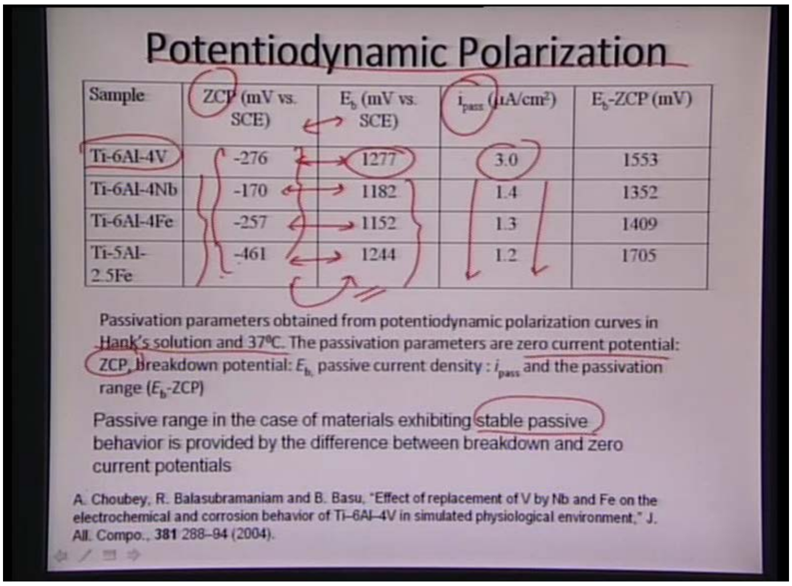
COF:
CP Ti: ~0.5 Ti-13Nb-13Zr: ~0.48
Ti-6Al-4V ~0.46; Co-28Cr-6Mo: ~0.40
Ti-5Al-2.5Fe ~0.3

A. Choubey, R. Balasubramaniam and B. Basu, "Effect of replacement of V by Nb and Fe on the electrochemical and corrosion behavior of Ti–6Al–4V in simulated physiological environment," J. All. Compo., **381** 288–94 (2004).

So, fretting wear basically, it was done using 10 newton load at 10 hertz and for a displacement distance of around 18 microns and they have done, they have gone up to around 10,000 cycles. All these studies were done under this stimulated body fluid environment. So, basically they found at the coefficient of friction to titanium 6 aluminum 4 vanadium lies between 0.46 to 0.50 and COF of titanium 5 aluminum 2.5 Fe falls within around 0.3 and they found that the major wear mechanism was tribomechanical abrasion, transfer layer formation and basically cracking.

So, there are three steps to it. One is the tribomechanical abrasion, then the transfer layer formation and then finally, the cracking. It is also that the coefficient of friction is very higher commercially pure titanium, which as to the order of 0.5, whereas it decreases in titanium 6 aluminum 4 vanadium. Marginally, it showed various from 0.46 to 0.50 and again, titanium 13 niobium 13 zircon showed around 0.48, whereas titanium 5 aluminum 2.5 Fe from 0.3 and cobalt 28 chromium 6, volume showed around 0.4 of coefficient of friction.

(Refer Slide Time: 36:58)



Potentiodynamic Polarization

Sample	ZCP (mV vs. SCE)	E_b (mV vs. SCE)	i_{pass} ($\mu A/cm^2$)	E_b-ZCP (mV)
Ti-6Al-4V	-276	1277	3.0	1553
Ti-6Al-4Nb	-170	1182	1.4	1352
Ti-6Al-4Fe	-257	1152	1.3	1409
Ti-5Al-2.5Fe	-461	1244	1.2	1705

Passivation parameters obtained from potentiodynamic polarization curves in Hank's solution and 37ºC. The passivation parameters are zero current potential: ZCP, breakdown potential: E_b, passive current density : i_{pass} and the passivation range (E_b-ZCP)

Passive range in the case of materials exhibiting stable passive behavior is provided by the difference between breakdown and zero current potentials

A. Choubey, R. Balasubramaniam and B. Basu, "Effect of replacement of V by Nb and Fe on the electrochemical and corrosion behavior of Ti-6Al-4V in simulated physiological environment," J. All. Compo., **381** 288–94 (2004).

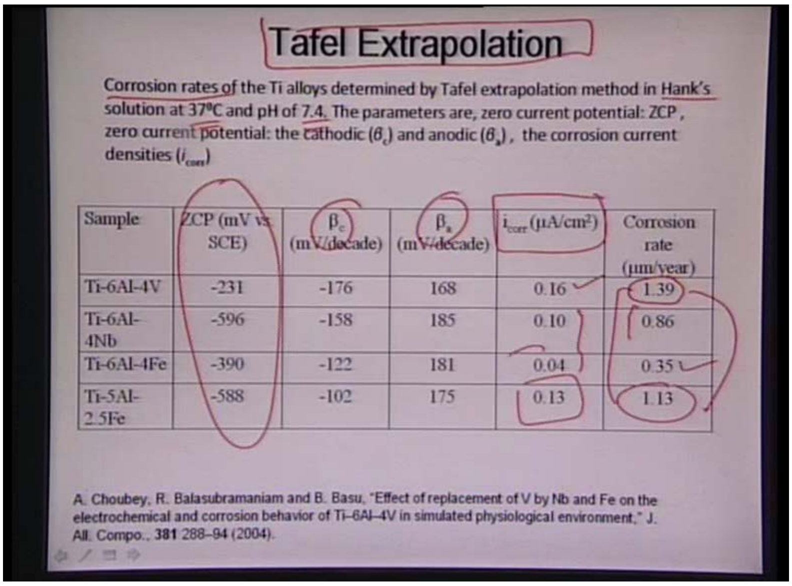
Coming back to the corrosion part of it that, the passivation parameters were obtained from the potentiodynamic polarization studies. So, they did again in the Hank solution at around at 37 degree centigrade and they found out the passivation behavior around at the zero current potential. So, ZCP, zero current potential and they saw that various values for different titanium alloys and the region between the breakdown potential in the zero current potential is a regime, where the material remains much more stable or passive. So, that stable passive region is being defined in the region of zero current potential and the breakdown potential.

So, in this if we just draw a comparison of all these four, we can realize which material is, which mean basically much more stable in nature. So, based on that, we can also see the approximate passivation current density which is around very high for titanium 6 aluminum 4 vanadium reduce marginally approximately half compared to the for the other alloys.

So, that is what is being observed here, that the passive regime in case of materials, which have a very stable passive behavior is basically been given by the difference between the zero current potential and the breakdown potential. That is what we are seeing out here that the breakdown potential is around, it is again very higher for the titanium 6 aluminum 4 vanadium, but it is approximately comparable for other alloys as well.

So, all these results are not so drastically different, but they are all comparable with one another.

(Refer Slide Time: 38:32)



Tafel Extrapolation

Corrosion rates of the Ti alloys determined by Tafel extrapolation method in Hank's solution at 37°C and pH of 7.4. The parameters are, zero current potential: ZCP, zero current potential: the cathodic (β_c) and anodic (β_a), the corrosion current densities (i_{corr})

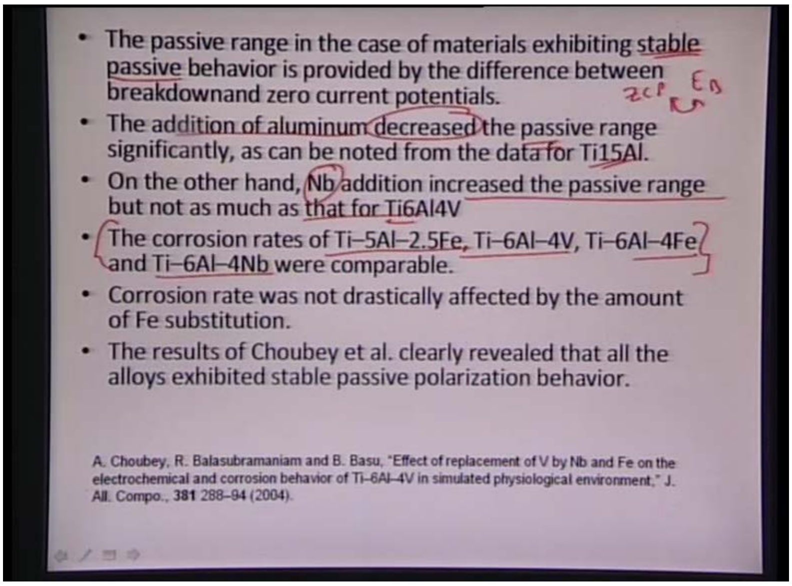
Sample	ZCP (mV vs SCE)	β_c (mV/decade)	β_a (mV/decade)	i_{corr} (μA/cm^2)	Corrosion rate (μm/year)
Ti-6Al-4V	-231	-176	168	0.16	1.39
Ti-6Al-4Nb	-596	-158	185	0.10	0.86
Ti-6Al-4Fe	-390	-122	181	0.04	0.35
Ti-5Al-2.5Fe	-588	-102	175	0.13	1.13

A. Choubey, R. Balasubramaniam and B. Basu, "Effect of replacement of V by Nb and Fe on the electrochemical and corrosion behavior of Ti–6Al–4V in simulated physiological environment," J. All. Compo., **381** 288–94 (2004).

Again, from the Tafel extrapolation, the corrosion rates got determined for the titanium alloys and we can see the corrosion rates in terms of micrometer per year or approximately, similar in nature, whereas titanium 6 aluminum 4 vanadium showed the best response. These others are much more comparable in nature and those were done again in the Hank solution at 37 degree centigrade at pH of 7.4.

All these parameters are zero current potential are being given here and the cathodic and the anodic current potentials are given out here and a corrosion current is also given out here, and the corrosion current was very higher for titanium 6 aluminum 4 vanadium and marginally, followed by this titanium 5 aluminum 2.5 Fe. Then, it was the least for the titanium 6 aluminum 4 vanadium and again, the passive regime in case of materials, they exhibit a stable passive behavior between the zero current potential and the breakdown potential or between these regimes, they show a much more passive region. We saw that the addition of aluminum basically decreases the passive regime. So, we had titanium 6 aluminum 4 vanadium.

(Refer Slide time: 39: 22)



- The passive range in the case of materials exhibiting stable passive behavior is provided by the difference between breakdownand zero current potentials.
- The addition of aluminum decreased the passive range significantly, as can be noted from the data for Ti15Al.
- On the other hand, Nb addition increased the passive range but not as much as that for Ti6Al4V
- The corrosion rates of Ti–5Al–2.5Fe, Ti–6Al–4V, Ti–6Al–4Fe and Ti–6Al–4Nb were comparable.
- Corrosion rate was not drastically affected by the amount of Fe substitution.
- The results of Choubey et al. clearly revealed that all the alloys exhibited stable passive polarization behavior.

A. Choubey, R. Balasubramaniam and B. Basu, "Effect of replacement of V by Nb and Fe on the electrochemical and corrosion behavior of Ti–6Al–4V in simulated physiological environment," J. All. Compo., **381** 288–94 (2004).

So, the addition of aluminum is basically decreasing the passive regime as we also saw at for that titanium 15 aluminum, but the niobium addition increases the passivation range but not as much as that of a titanium 6 aluminum 4 vanadium. Again, all the corrosion rates for all these materials which we saw earlier, whether it was titanium 6 aluminum 4 vanadium, 6 aluminum 4 Fe or 5 aluminum 2.5 Fe or 6 aluminum 4 niobium, they are all comparable. As we saw earlier, that the corrosion rates are basically given out here and they are not too drastically different in terms of around 0.5 to 1.5 micrometer per year.

So, they all show a much more stable region and we see that this addition of this particular aluminum is basically responsible for the enhanced passivation regime, like all these are showing much more vast passivation regime out here. So, that is what is being the role of aluminum. That aluminum is basically deteriorating the passive regime, whereas niobium is tending to increase the passivation regime. As we can see in this previous case, that once we start adding the niobium out here, we can see much more the difference between the two regimes out here. So, overall we see that the corrosion rate is not so different for all these materials, even when we are adding certain ion to it and they also clearly reveal that the stable passive polarization behavior is existence between zero corrosion potential as well as the breakdown potential.

So, coming back to the titanium alloy, the overall adjust of the titanium alloy, they are mostly ACP in nature and then, we tend to add alloying elements such as aluminum which is again ACP stabilizer or the alpha space stabilizer. Then, we add vanadium, which is a beta phase stabilizer or the BC stabilizer.

So, there are two ways we can synthesize particular material. We can heat it above 1000 degree centigrade and let the material cool slowly, but that consists of very huge grains or they tend to precipitate alpha in the beta grains and beta grains are very coarse in nature. From that we can get a Widmanstatten structure, but since the grains are gone to grow to a large extent as well as, we are getting a very needle kind of a structure, this overall macrostructure does not appear good and then it is generally showed very poor strength.

So, to avoid that particular part, we take the material to lesser than 1000 degree centigrade and we let the alpha dominate in this particular regime and then, we see certain nucleation of this beta precipitated, which is again this is see nature. So, we see very fine grain structure with very nicely response beta in that. So, that essentially gives that to a two phase microstructure which is very fine microstructure 10 to 20 microns with beta of around 1 to 2 to 1 to around 5 microns in size.

So, that gives a very uniformly dispose microstructure and that is superior. It is a mechanical property in terms of yield strength and in terms of its fatigue strength. So, what we can see is that heat treatment is very essential or key component in terms of altering the mechanical properties. So, we increase the fatigue strength by order of by or approximately two times. Once we do a control heat treatment to the particular material, at the same time we realize that the surface coating is also one of the key components to the surface, one which comes in direct contact with the body environment.

So, we see that we need to have a very good wear resistance; we need to have a corrosion resistance and at the same time, should be biocompatible enough. So, some coatings can also be applied to the ceramic coatings can also be applied. Also, we can do certain treatment, chemical treatment to it because the surface of titanium, so that it becomes much more compatible with the body and then, cells can really start with growing on to them.

That is also one key feature of utilizing titanium implants that we can take, make use of that titanium oxide, which grows on the surface. Then, make a chemically active and then also treat it thermally. So, we can achieve a very good biocompatible surface out here and we also realize that the aluminum tends to decrease the passivation region, whereas the niobium tends to increase it to a little extent and that is what the overall corrosion and wear behavior of this titanium alloy in titanium 6 aluminum 4 vanadium alloys. So, basically I end my lecture here. Thanks a lot.