Introduction to Biomaterials

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Module No. # 01

Lecture No. # 16

Ti Alloy

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

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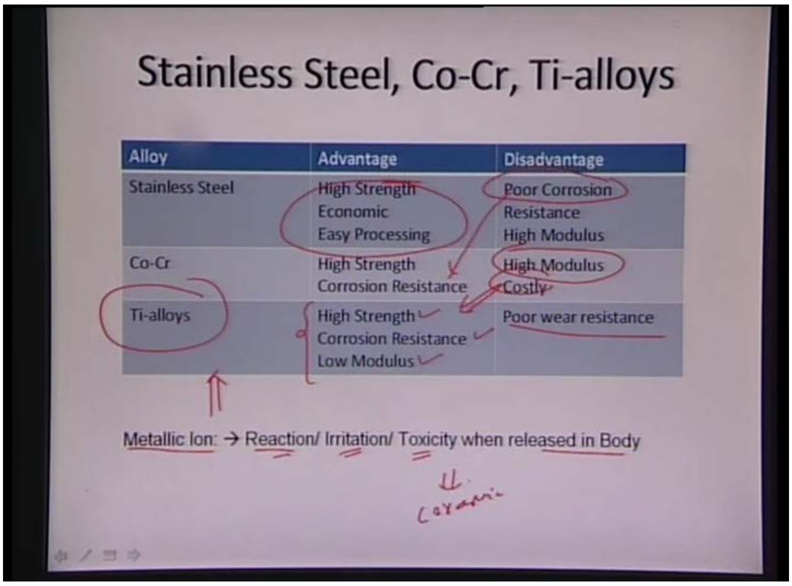

Stainless Steel, Co-Cr, Ti-alloys

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 a easy processing, but the problem mainly with that stainless steel, 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 very high modulus, then essentially what happens, the bone will start thinking oh it is, I do not need to be here and then, it is start getting with reabsorbs into the body.

So, that is the reason we want to come back to a material which has little load over lower modulus and that thing is being sufficed by titanium alloys.

So, they provide a good combination of high strength, good corrosion resistance, low modulus, but the only problem is that titanium alloys is that, they have very poor wear resistance. So, to counteract the poor wear resistance to generate titanium alloys, they need to be supplied with some sort of a surface coating. So, surface coating, they take care of the wear part. So, they try to enhance the surface wear resistance of the titanium implant. 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 has very poor wear resistance and then we can also apply some sort of a coating which can assist some bone integration on to it surface. So, that coating can be more of ceramic in nature, that is hydroxyapatite and then, once the coating of hydroxyapatite base 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 implant with superior wear properties. Also, it can provide a base for cells to grow and get adhere and proliferate on the implant surface. There is one more problem with titanium alloy titanium 6 aluminum 4 vanadium is that, it is metallic ion concentration and that basically can tend to react, irritate or induce some toxicity where it is releasing 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 coating that has a barrier; they do not allow the ions to flow easily from the implants surface to the surface of the material. Commonly, the titanium alloys, they are the two common, very common titanium alloys which are predominant in the medical industry or commercially pure titanium, which is approximately 89.9 percent to 99 percent plus purity.

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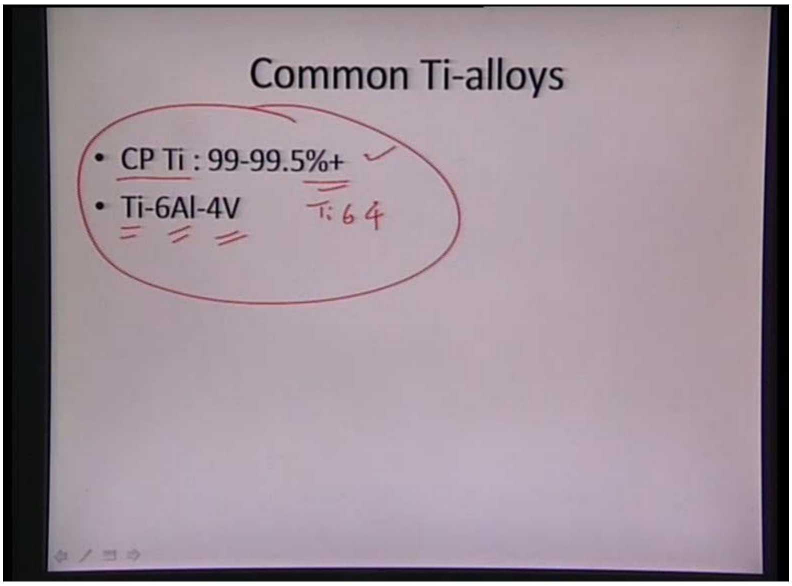

Common Ti-alloys

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

Ti 6 4

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, it is also called Ti-6Al-4V. So, it is also called Ti-6-4 for easiness in the use, but these are the two some very commonly used titanium alloys which are utilized in the biomedical industry.

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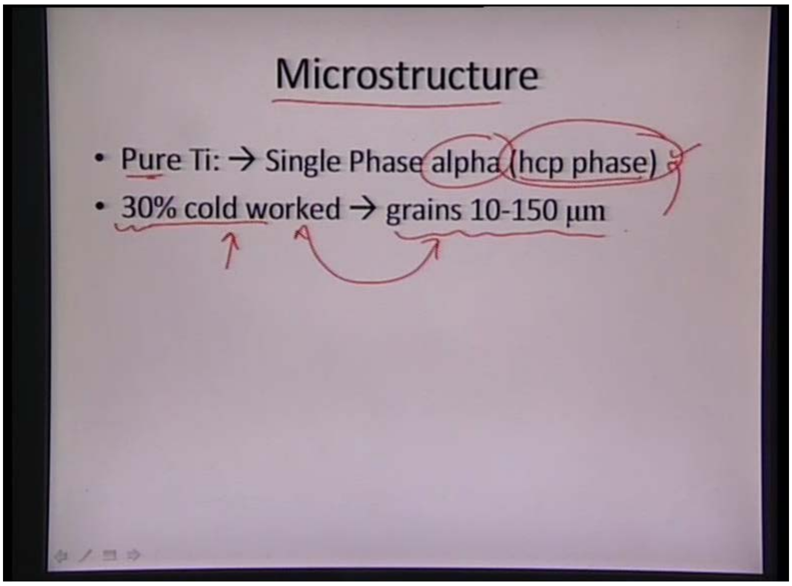

Microstructure

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

Coming to the microstructure part of it, the pure titanium, it has basically hexagonal HCP phase and the phases called alpha phase. So, pure titanium appears more, it is more of a single phase material and it is HCP and orient to the limited HCP slip place which are available in HCP crystal. It has very limited processibility in terms of; it has very limited number of slip place. So, that is generally very difficult to process as such. Again, this particular titanium alloy is generally cold work to achieve grains in order of 10 to 150 micrometer in size. So, ideally we can get a single phase structure in titanium alloy and to basically induce much more strengthening, we go with the cold working point. An 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 micrometer in diameter.

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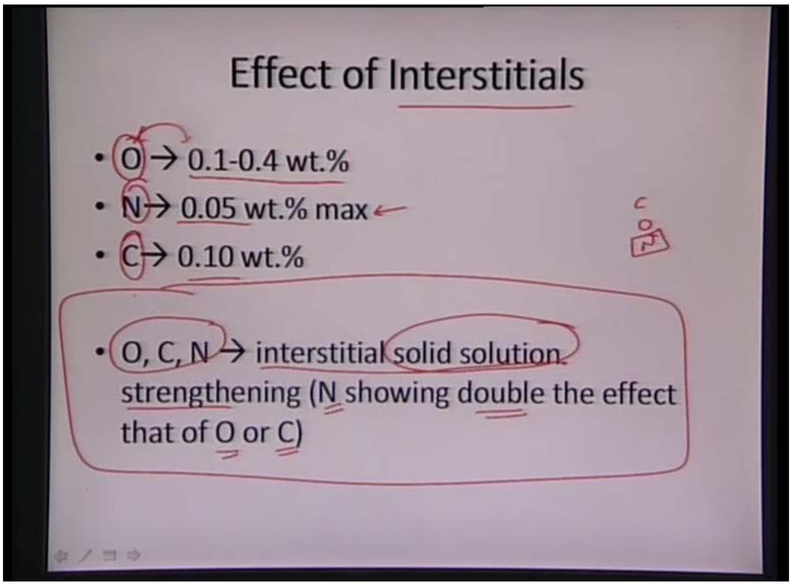

Effect of Interstitials

- O → 0.1-0.4 wt.%
- N → 0.05 wt.% max
- C → 0.10 wt.%
- O, C, N → interstitial solid solution strengthening (N showing double the effect that of O or C)

There can be addition of secondary interstitials into the titanium and those can be either, oxygen, nitrogen or carbon. They go into the interstitials size of the titanium and from that, we can have various combinations. There are certain grades which basically differentiate the titanium alloy. They go from grade 1, grade 2, grade 3, grade 4 depending on the oxygen contain 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 this interstitials is, so that we can achieve interstitials solid solutions strengthening.

So, we can see that when the carbon or oxygen or nitrogen with their in the interstitials sites, basically they reduce solid solution strengthening of the titanium alloy. It has also been observed by researchers, that nitrogen shows at the approximately double the effect of either oxygen or carbon. So, if we have nitrogen setting in the interstitials, it will provide much more strengthening effect than comparison to that of our oxygen and carbon. 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 are this, go and sit in the interstitials site and nitrogen shows approximately double the effect of oxygen or carbon to provide strengthening or the solid solution strengthening, interstitial solid solution strengthening.

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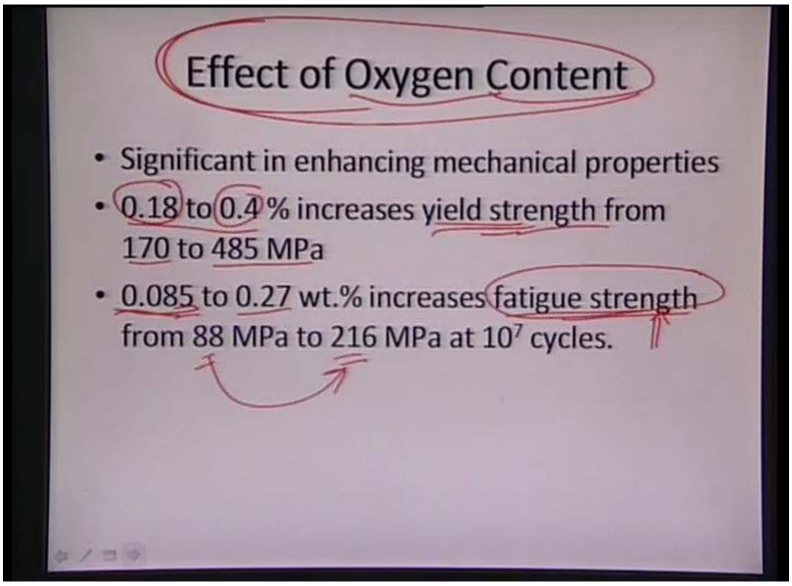

Effect of Oxygen Content

- 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 enhancing the mechanical properties, 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 to two and half times improvement, it can show in the yield strength just 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 start 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 around 0.27 weight percent, we will also see increase in the fatigue strength. So, we see that fatigue strength is increasing approximately from 88 to 216. It is also showing approximately, if we increase that oxygen content, approximately double or triple same type of effect, we can see in the fatigue strength as well. So, we can realize that the oxygen content is very 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 increasing in the yield strength or the fatigue strength of the particular titanium alloy.

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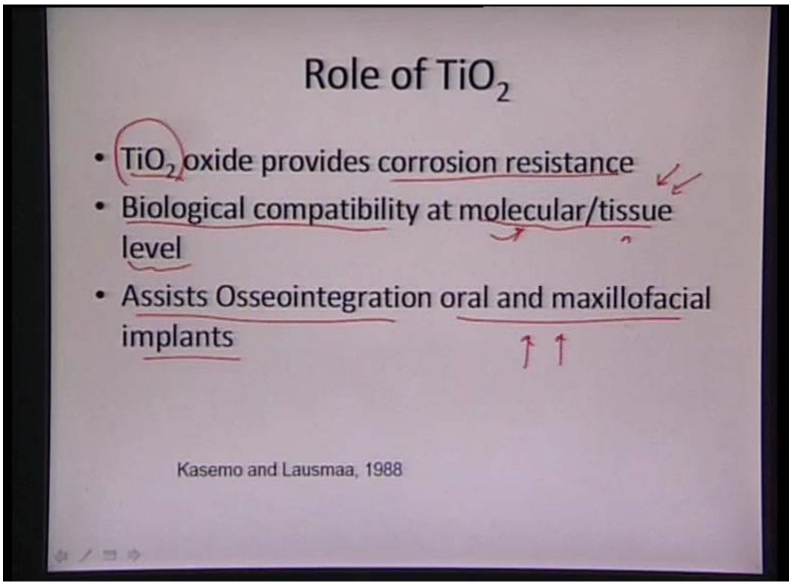

Role of TiO_2

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

Kasemo and Lausmaa, 1988

The corrosion resistance comes in the titanium alloy because of the presence of this titanium oxide layer. So, titanium oxide layer provides as a barrier for the surface to interact with the titanium implant and this titanium oxide is responsible for rendering the corrosion resistance with the tissue level. Because of its similarity, it can allow that cells or tissues to grow on its surface without inducing any toxic effects. So, that biological compatibility is available even at molecular state or even at the tissue level, so that tissue finds the very friendly environment on the titanium oxide surface because it is no more titanium.

Titanium is basically covered with the improvised layer of titanium oxide. So, there is no release of titanium ions to this particular titanium oxide. Titanium oxide is much more bio-friendly, is with bio alert in nature and that does not induce some irritation or toxicity effects 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 is to impart much corrosion resistance even in the very severe body fluid environments and again it can also impart much biological compatibility, both at molecular level as well as the tissue level. Also, researchers have found that (()), 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. It is much more bio-friendly in nature and it allows osseointegration, oral and also a maxillofacial implants.

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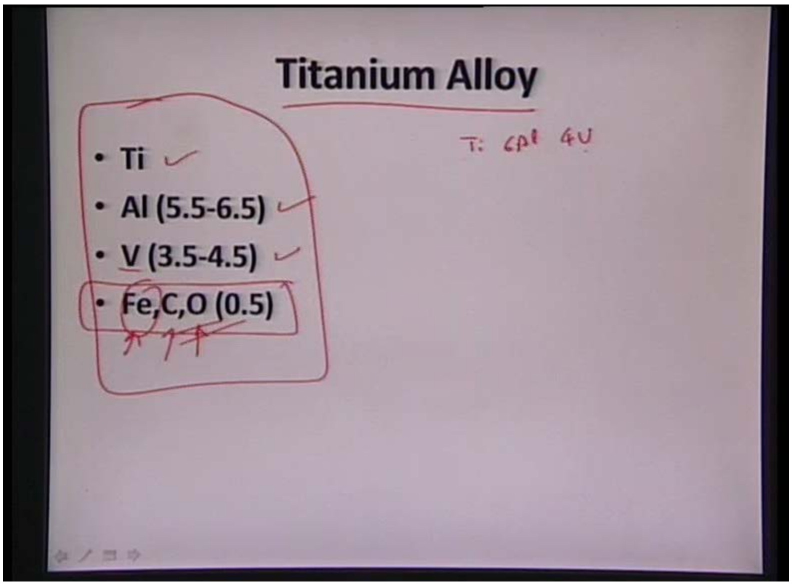

Titanium Alloy

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

Ti: 6Al 4V

Coming to the titanium alloy, generally the titanium itself is not that stronger in nature, so it also needs certain reinforcement because titanium is the single phase material and if we start making it dual phase material, so instead of having only alpha or the HCP phase, if you start inducing the secondary phase, we can also get strengthening from the secondary precipitate. Why? Because it will also impart the impediment to the dislocation motion and 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 processing part has basically enhanced and the same time, the strength part can also get enhanced because of the dual phase microstructure.

So, in the titanium alloy, we have bases 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 interstitials, such as carbon and oxygen. So, we can 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 very popular material as for the biomedical implant as a biomedical implant material and it consists of aluminum around 6 percent and vanadium of around 4 percent and rest is around carbon, oxygen and so on.

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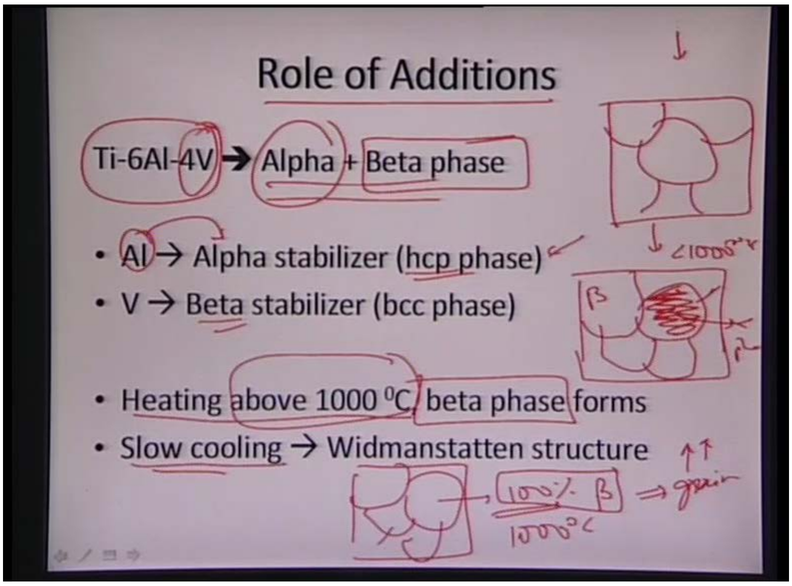

Role of Additions

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 on to titanium 6 aluminum 4 vanadium, it forms a dual phase microstructure. So, alpha comes basically from the titanium part. At the same time, alpha is also being stabilized by aluminum. So, aluminum also acts as the alpha stabilizer. It renders making HCP phase much more stable, but the presence of vanadium helps forming a beta phase. So, we see this titanium 6 aluminum 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 had already single phase which was nothing, but only alpha. In this case, we see that we have dual microstructure, so we are seeing a kind of a dual microstructure out here and in this case, some certain (( )) 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 very high fatigue strength, when we have a dual phase microstructure. That is advantage with achieving a new thing, the secondary alloys such as aluminum and vanadium. So, impart much more increase in the yield strength and the fatigue strength of titanium alloy in itself.

One more thing which happens to 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, this is stabled at high temperature. So, once we go above 1000 degree 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 we start cooling it very slowly, then what will happen that the material is basically being retained at very high temperature for 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 that will tend to see something called Widmanstatten structure. So, in the Widmanstatten structure, we basically have structure like this, I will just draw it here. We see a structure in which, initially we would have only beta grains once it is heated at high temperature. So, in this case, we have greater than 1000 degree centigrade. We see completely 100 percent beta and as soon as we start cooling it down slowly, we will see the increasing 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 grains, which were stable at more than 1000 degree centigrade and we see nucleation of alpha phase. So, in this particular case, we had larger beta grains and in that, we see a needle like secondary alpha phase. This structure is not that good. Why? Because it can be very highly brittle and because it is a grain size, it is very huge and also it is more like a needle structure. So, needle, it means it can be used in very high stress concentration factor. So, that is the reason, this structure is not so preferable.

So, we see very huge beta grains 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 starts precipitating. Since, it is the needle like structure, this structure can induce very high stress concentration factor near its strip because it is a needle like structure. So, that is the reason it can be very deleterious. So, we may not achieve that sort of a strengthening or 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 slow cooling is inducing some deleterious effects in this particular material.

The grain sizes, they can basically be more than given 500 microns and at this particular grain size, the properties, mechanical properties will be very inferior because of the (()) relationship. Our grain sizes are to the order of around more than 500 microns, so the overall mechanical properties may be such as yield 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 letting the beta to stabilize. Then, we are allowing the alpha phase to form an equilibration, so we are doing a very 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 and 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 inducing this negative effect.

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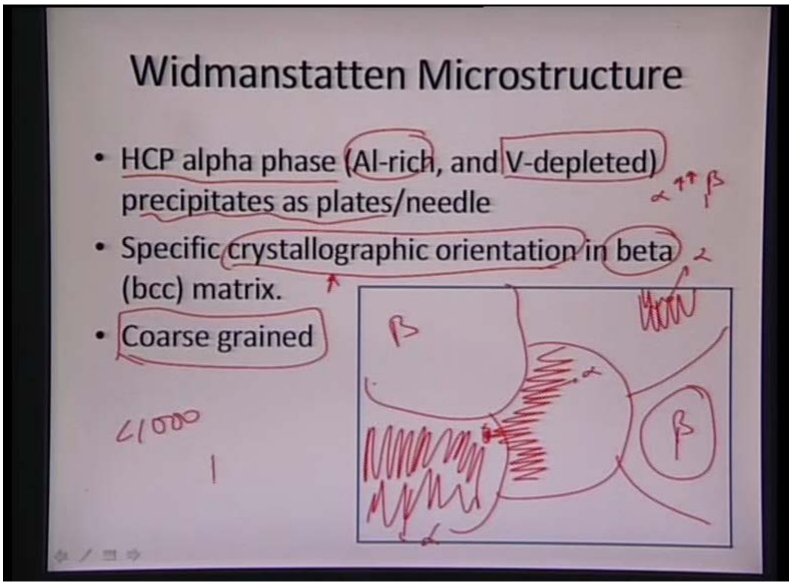

Widmanstatten Microstructure

- 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 and again this is V-depleted in the vanadium part. It starts precipitating as the plate or needle. So, we see that we had grains like this for the beta and then, in that, we see the nucleation of this alpha phase, which can start nucleating at within like this. Then, we have this beta phase and then again, we will see alpha phase nucleating because alpha phase will be much more stable at less than 1000 degree centigrade, we will see more of the grains which are forming alpha now. So, we will have much more regions which will start 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.

Then, we start single formation of alpha structure. This is much more needle 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 grains. 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 is staying for the whole heat treatment for couple of hours.

So, that is what the problem with this particular material is. We are taking 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 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. I will 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 a very poor structure.

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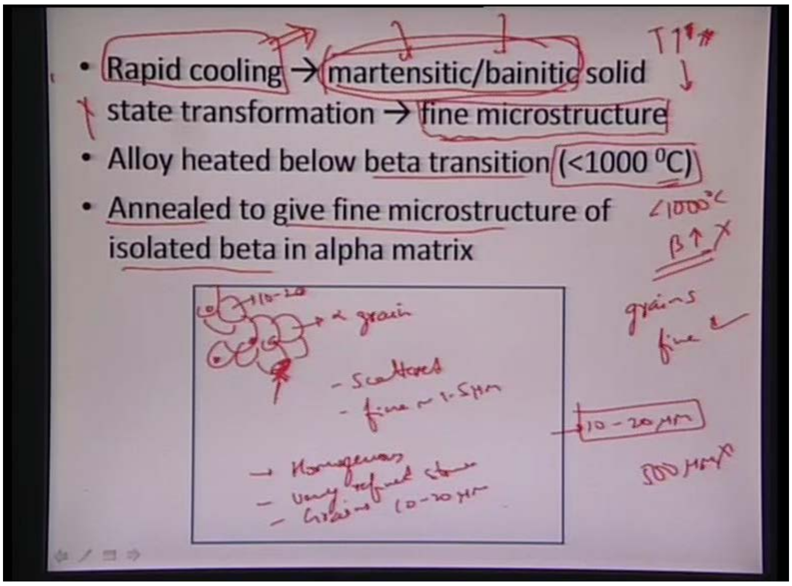

- Rapid cooling → martensitic/bainitic solid state transformation → fine microstructure
- Alloy heated below beta transition (<1000 ^{0}C)
- Annealed to give fine microstructure of isolated beta in alpha matrix

So, to avoid that particular part what can be done? We can do a rapid cooling. Rapid cooling, it is basically a martensitic or bainitic type solid state transformation and since, we have very rapid cooling, we can also achieve very fine microstructure. That is the advantage with this rapid cooling is that, instead of very course 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 for very long time, but temperature is not high anymore. We are doing a very rapid cooling. So, we go to excess of 1000 degree centigrade, but we cool the material very rapidly and that rapid cooling induces martensitic or bainitic solid state transformation. Again, rapid cooling also induces very fine microstructure and again, the alloy is heated or cool below the beta transition.

So, we are not letting this particular material go above 1000 degree centigrade. So, we are letting this transition happen below 1000 degree centigrade. So, we are hitting the material to lesser than 1000 degree 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 the grains to get coarsed. So, grains remain fine and they are retained as such. So, we are not letting the grain get coarsed because we are basically hitting them much below 1000 degree centigrade. 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 large extent. So, we see very fine grains which can be formed and these fine grains, they are to the order of around 10 to 20 microns.

So, instead of going up more than 500 microns, they are no more 500 micrometers in diameter. They remain in the 10 to 20 micrometer 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, it is again scattered and it is again very fine. Fine 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 alpha, so the beta, which is basically getting nucleated at high temperature, it is again very fine and it is scattered throughout.

So, we see very homogenous structure. Homogenous 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 degree centigrade. We keep the material lower than 1000 degree centigrade and then, we do annealing or rapid cooling. Rapid cooling is basically retaining those fine alpha grains and we see some precipitation of the beta grains within the alpha grains.

So, we have alpha grains round in the order of 10 to 20 micrometers and then, beta is getting precipitated here and there. Again, the size of beta precipitate is again couple of microns. So, overall what we get is, very uniform structure, a very nicely disperse beta in the alpha matrix. Now, we do not have any segregation or Widmanstatten structure anymore and the grains. Grains themselves are now limited size of around 10 to 20 micrometers. So, overall properties, they grow multi four because of absence of this negative structures, such as the Widmanstatten structure or the coarse grain. So, the fine grain materials all now induce this (()) relationship. Because of the (()) relationship, we can get much superior properties, mechanical properties which have been stated in the earlier lectures also.

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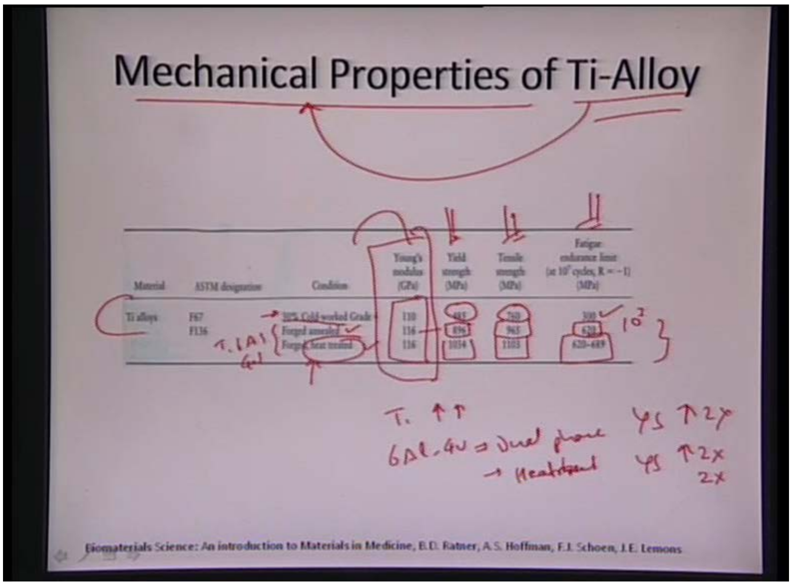

Mechanical Properties of Ti-Alloy

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 4	110	485	760	300
	F136	Forged annealed	116	896	965	620
		Forged heat treated	116	1034	1103	620–689

T. 6Al 4V

10^7

Ti ↑↑

6Al-4V ⇒ Dual phase YS ↑2x

→ Heat treat YS ↑2x

2x

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

One thing is basically seen that titanium alloys, the young's modulus does not change much even with certain additions and for a commercially pure titanium, this is cold work to around 30 percent. You see yield strength which is to the order of around 485, tensile strength of around 760 mpa and it has fatigue erroneously limit of around 300, but as well as we start adding certain alloys to it, like in case of titanium 6 aluminum 4 vanadium, that is that material is forged annealed and heat treated. So, we can see that one side is annealed, we can see increase in the yield strength up to around 900 megapascals, tensile strength of around 1000 mpa and fatigues strength is almost double. So, at the 10 power 7 cycles. Again, control heat treating can increase. It is yield strength to around 1034 megapascals, which is more than a gigapascal. Tensile strength is also increased by certain extent around 1.1 gigapascals and fatigue strength is also increased to a certain extent.

So, we can see how much the role of the heat treatment can be utilized in its particular processing of titanium alloy to achieve enhance mechanical properties, that is what it is like titanium alloy, we are seeing certain properties. Once we add 6 aluminum 4 vanadium, we see a dual phase microstructure and that dual phase microstructure is basically, assisting in the increase of yield strength which is almost 2 times and then, again heat treatment, control heat treatment can again increase the yield strength by that matter of time. Again, the fatigue (( )) limits can also be increased by around 2 times, so that is the way in which we can manipulate the properties of titanium alloy via certain secondary additions and as well as performing some heat treatment by utilizing heat treatment of the titanium alloy.

So, those are the advantageous of utilizes titanium alloy and performing the heat treatment because we can achieve very superior yield strength and tensile strength and the fatigue strength, though the Young's modulus remains same, approximated it is stimulated. This is not changed much, but the enhancement in the yield strength, tensile strength and my fatigue strength is just phenomenon.

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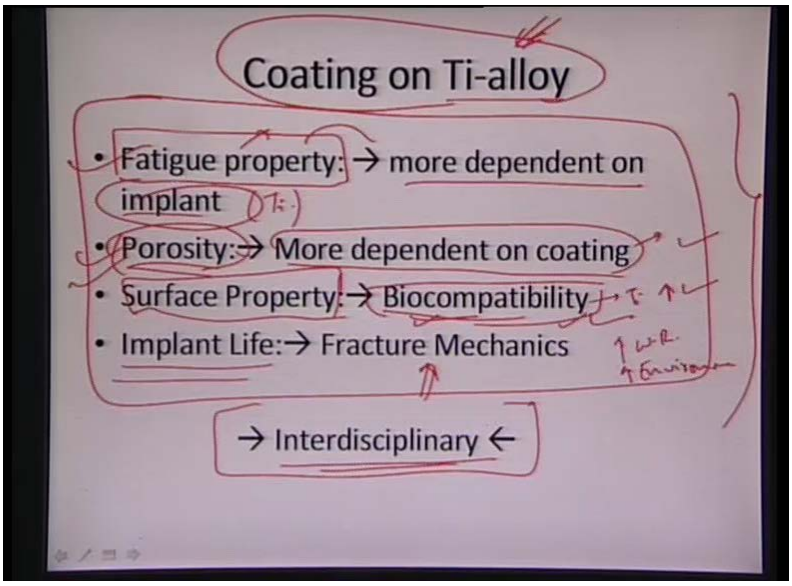

Coating on Ti-alloy

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

→ Interdisciplinary ←

Again, titanium alloy as we learnt earlier that titanium alloy, it has a very poor wear resistor. Either, same time if we want to have a 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 ceramic, so they do not have enough yielding which can happen in the material. So, we see that the fatigue properties are much more dependent on the titanium alloy.

So, that part or we can see that fatigue property is more dependent on the implant or the titanium alloy, which forms the implant. To improve the fatigue property, it has only titanium alloy which is anything responsible out there. So, we need to perform certain heat treatments as we saw earlier, that we need to perform control heat treatment, need 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 have fatigue strength, overall 300 and megapascals at 10 power 7 cycles, but if you take a titanium alloy and properly heat, rate can go up to 600-700 mpa for same life cycles. So, that identity essentially tells us, that we have to utilize a superior grade of titanium, if you want to achieve a very high or the enhanced fatigue properties because that is mostly dependent on the implant. Implant is one which is to take the overall load.

Secondly, there is some more term called porosity and that is more dependent on the coating part because porosity, it essentially allows us to select what is the manner in which the surrounding environment of the body will interact with the implant material. Coating itself is bad. If coating is not good, not adhering to the cells, cell may not tend to adhere on the implant and will see a failure or there would not be any bonding 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 that we need to have enough porosity that cells can come and they can adhere on to the surface and they can clean themselves on to the porosity which is available to them. Then, form a strong bone 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. Again, this surface coating is highly responsible in terms of the biocompatibility. So, surface is the one which comes in direct contact with the cells, so the surface itself is not biocompatible. We will see toxic effects, cells may not tend to adhere to the surface, cells may not proliferate and cells may not grow at all on the surface.

So, we see that surface property is highly essential in terms of dictating 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 and again, the implant life itself depends on many aspects, such as it can depend on the fatigue property, it can depend on the porosity, and it can depend on the biocompatibility. Again, all these aspects are mutli-disciplinary in nature. A metallurgist will come and find out about the material, mechanical engineering will come out and then take much more about the fatigue property. Then, a biologist will come and 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 very 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 induce some sort of porosity under the material. They can enhance the wear resistance of the material, so they have to be the ones which are much more seems the direct environment. So, the coatings are one of the very essential components of the implants as such.

So, this overall study of making a particular alloy as an implant, it is interdisciplinary in nature. So, this is what is the underlining part that all these aspects should be taken are 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 or the fatigue, one material can withstand. Coming to its biocompatibility part as whether the material itself is biocompatible or not.

So, we need to impart certain coating provide sing about the wear resistance to at sing about the corrosion resistance. Again, we need some sort of coatings which can be 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 cling on to it or not, or seeing about its biocompatibility, seeing about the mechanical part whether the fracture will occur prolonged or it will come very shortly. So, those all parts make this particular study a interdisciplinary in nature and that is what makes it much more complicated.

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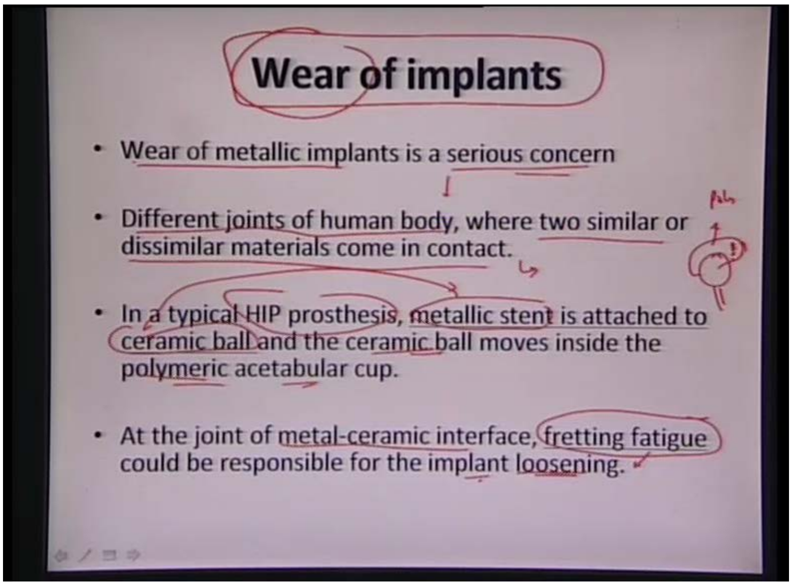

Wear of implants

- 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 multi-disciplinary 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. Perhaps there is some movement between the two, obviously the material will undergo some sort of a wear, like we have acetabular cups and we have a ball and socket joint.

So, in there we can see here, overlay between metallic and metallic surface in a polymeric or ceramic surface. So, once we have to dissimilar the metals which are being closer to one and another, we see there will be definitely some wear on to the particular interface. So, again wear of metallic implants is one of the very serious concerns because one set starts releasing some debri on to, while it get in abbreviated or getting worn out. So, those ions will start getting released into the body and again, this way will occur at different joint of the human body and once it is being implanted into the body, there is hardly any control.

So, all those debris which is being generated that was trying to accumulate somewhere, so those are being just raised into the blood and that is we do not have any control after that. So, we need to have a material which will have very superior wear resistance, once it is being implanted into the body. So, we need to see that, wherever two similar or dissimilar metals are 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 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 interface between the ceramic ball and the metallic stent, this some rated movement between the ceramic ball and again it is moving either in the polymeric acetabular cup or we can see that a ball is made up of some material like 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 and basically between the metallic and ceramic interface, 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 interfaces between metal and ceramic interface 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 implant back into the body and basically do one more surgery. So, that particular material is 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.

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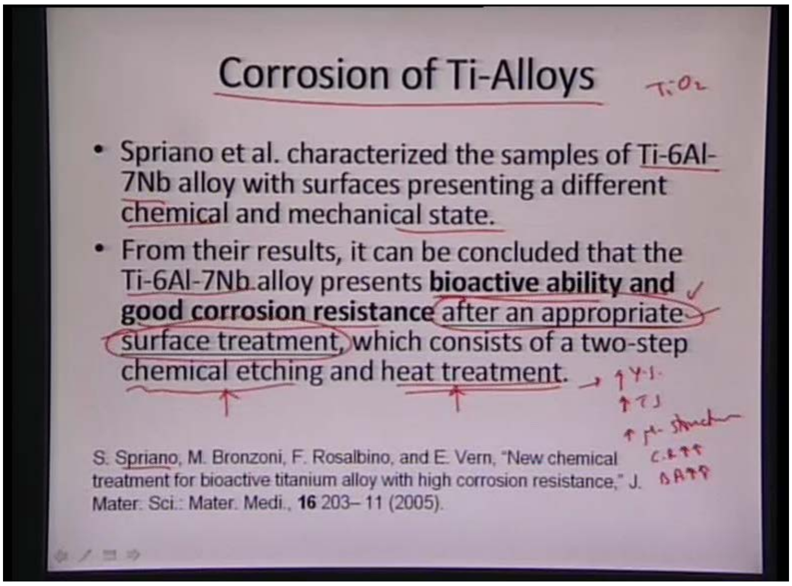

Corrosion of Ti-Alloys

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. ↑ TS ↑ 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).

Coming back to one more important property of this titanium alloys is about its corrosion resistance. So, corrosion of titanium alloys is also one of the very critical parts because like, generally we utilize titanium alloy which generally tend to be good corrosion resistance because of the formation of TiO2 layer on its surface. So, there is a group of Spriano which have characterizes sample of titanium 6 aluminum 7 niobium alloys and with surfaces which were present toward different chemical and mechanical states. From that they have found that titanium 6 aluminum 7 niobium, it presents a bioactive ability and good corrosion resistance only after 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 a utilizing proper wear resistance, corrosion resistance, at the same time having it much more biocompatibility. So, that it can take the overall aspect of its biocompatibility 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 and 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 read out by the Spriano that only after the appropriate surface treatment is given. Why? Surface treatment is so important because surface is the one which will come in 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 Latina cells. They strict on to itself, latina cells grow on itself and proliferate to form certain networks itself. So, that is what the overall study which was carried out by the Spriano.

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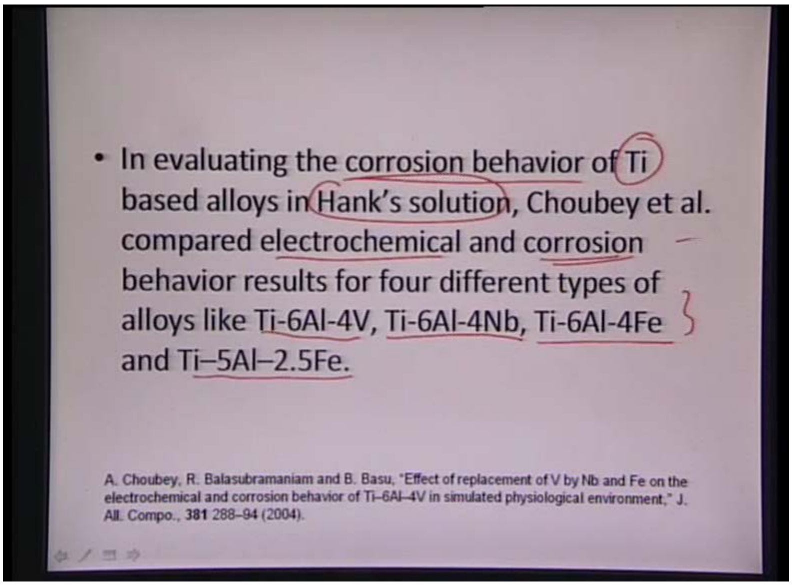

- In evaluating the corrosion behavior of Ti based alloys in Hank's solution, Choubey et al. compared electrochemical and corrosion behavior results for four different types of alloys like Ti-6Al-4V, Ti-6Al-4Nb, Ti-6Al-4Fe and Ti–5Al–2.5Fe.

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).

This is one more group of Choubey, through which have utilized falling the corrosion behavior of titanium based alloys. So, they took a couple of alloys, which is titanium 6 aluminum 4 vanadium, titanium 6 aluminum 4 niobium, titanium 6 aluminum 4 Fe, titanium 5 aluminum 2.5 Fe. So, they have taken a couple of four different types of alloys and basically found its behavior in the Hank's solution. So, then they have compared what is the electrochemical and the corrosion behavior of all these alloys for different conditions. So, that is what they have found out.

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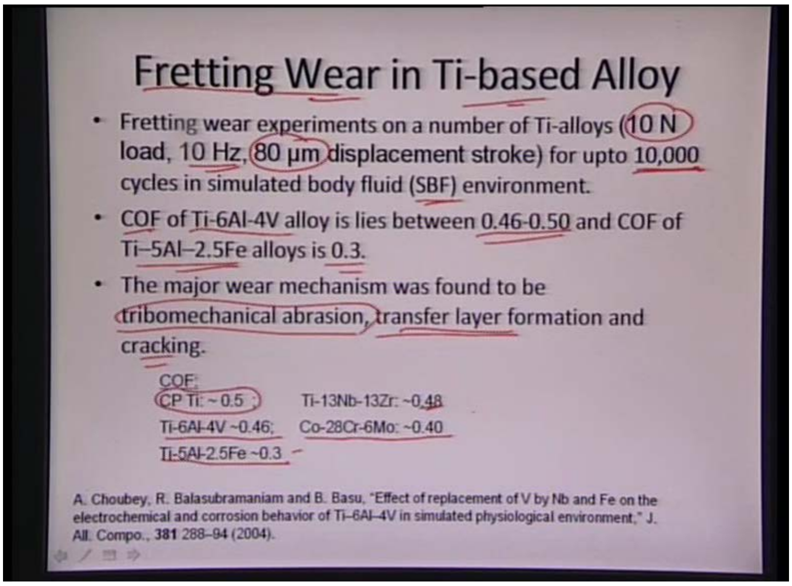

Fretting Wear in Ti-based Alloy

- 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).

At the same time, they also have done fretting wear of the titanium based alloys. So, fretting wear basically, it was done using 10 newton loads at 10 hertz and for a displacement distance of around 18 microns. They have done, they have gone up to around 10,000 cycles and all these studies were done under the stimulated body fluid environment.

So, basically they found that the coefficient of friction for titanium 6 aluminum 4 vanadium lies between 0.46 to 0.5, whereas that of, 5 aluminum 2.5 Fe falls within around 0.3. 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. That also tells that the coefficient of friction is very high for commercially pure titanium, which is to the order of 0.5, whereas it decreases in titanium 6 aluminum 4 vanadium marginally.

It showed various from, 0.46 to around 0.5 and again titanium 13 niobium shown around 0.48, whereas titanium 5 aluminum 2.5 Fe around 0.3 and cobalt 28 chromium 6 showed around 0.4 of coefficient of friction and coming back to the corrosion part of it, that the passivation parameters were obtained from the potentiodynamic polarization studies.

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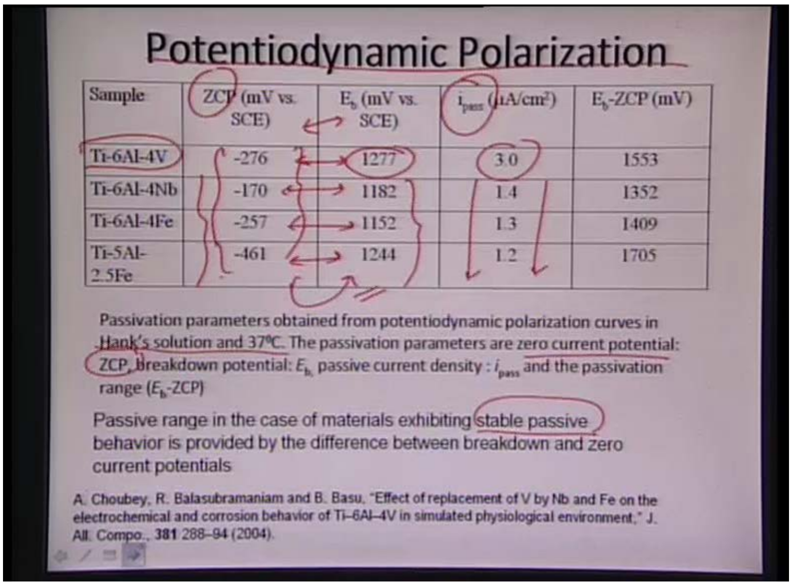

Potentiodynamic Polarization

Sample	ZCP (mV vs. SCE)	E_b (mV vs. SCE)	i_{pass} (μA/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 37°C. 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).

So, they would read again in the Hank's solution at 37 degrees centigrade and they found out the passivation behavior around at the 0 current potential, it was ZCP, 0 current potential. They saw that various values for the different titanium alloys and the region between the breakdown potential and the 0 current potential is the region, where the material remains much more stable or passive. So, that stable passive region is being defined in the region of 0 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 basically much more stable in nature. So, based on that, we can also see the approximate the passivation current density, which is around very high for titanium 6 aluminum 4 vanadium. It is marginally, approximately half as they compared for the other alloys.

So, that is what is been observed here that the passive range in case of materials, which have a very stable passive behavior is basically been given by the difference between the 0 current potential and the breakdown potential. That is what we are seeing out here that the breakdown potential is around, it is again very high 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 all are comparable with one another.

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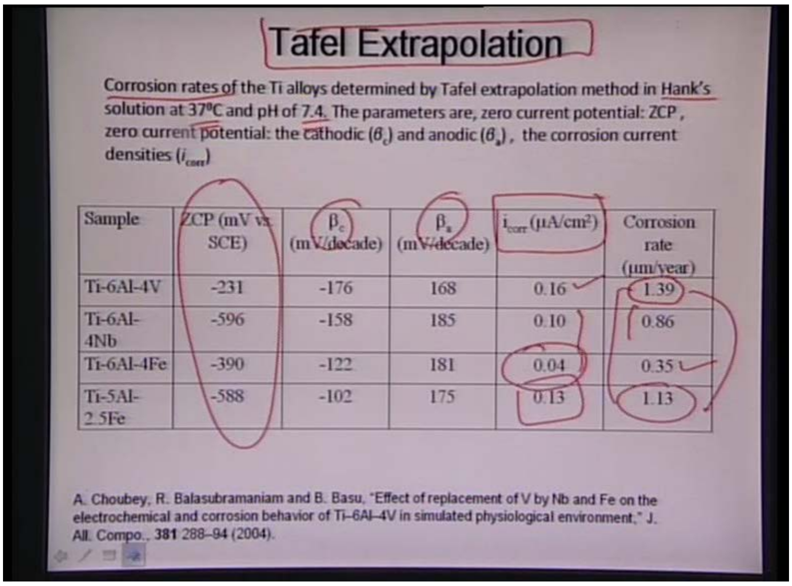

Tafel Extrapolation

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/cm²)	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 Tafel extrapolation, the corrosion rates were determined for titanium alloys and we can see the corrosion rates in terms of micrometer per year are 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 and pH of 7.4 and all these parameters of 0 current potential are being given here. The cathodic and the, sorry cathodic and the anodic current potentials are given out here and the corrosion current is also given out here. The corrosion current was very high for titanium 6 aluminum 4 vanadium, and marginally followed by this titanium 5 aluminum 2.5 Fe and then, it was the least for the titanium 6 aluminum 4 vanadium.

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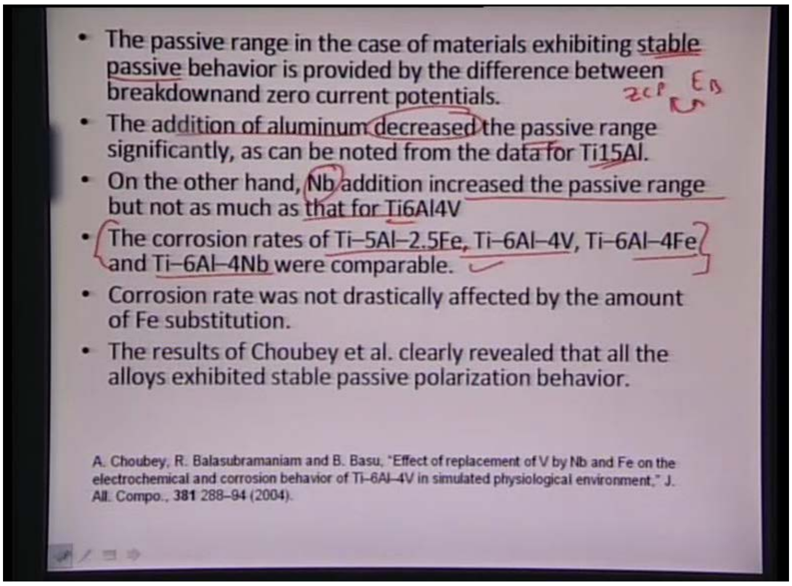

- The passive range in the case of materials exhibiting stable passive behavior is provided by the difference between breakdownand zero current potentials.
- The addition of aluminum decreased the passive range significantly, as can be noted from the data for Ti15Al.
- On the other hand, Nb addition 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.

zcp E_B

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, the passive range regime in case of materials, they exhibit stable passive here between the 0 current potential and the breakdown potential and between these regime, they show a much more passive region and we saw that the addition of aluminum basically decreases the passive range.

So, we had titanium 6 aluminum 4 vanadium, so the addition of aluminum is basically decreased in the passive range as we also saw it for the titanium 15 aluminum. The niobium addition increased the passive passivation range, but not as much as that of a titanium 6 aluminum 4 vanadium and 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 so 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 region regime, like all these are showing much more vast passivation region regime out here. So, that is what is being the role of aluminum. That aluminum was basically detonating the passive regime, whereas niobium is trending to increase the passivation regime as we can see in this previous case, that once we start rating the niobium out here, we can see much more, that is difference between the two regimes out here.

So, overall we see that the corrosion rates are not so different for all these materials, even when we are adding certain iron to it. They also clearly reveal that the stable passive polarization behavior is existent between 0 corrosion potential as well as the breakdown potential. So, coming back to the titanium alloy, the overall legist of it, titanium alloy, they are mostly HCP in nature and then, we tend to add alloying elements aluminum which is again HCP stabilizer or the alpha phase stabilizer. Then, we had vanadium, which is a beta phase stabilizer or the BCC stabilizer.

So, there are two ways we can synthesize this particular material. We can heat it above 1000 degree centigrade and let the material cool slowly, but that tends to form very huge grains or they tend to precipitate alpha in the beta grains. Beta grains are very coarse in nature and from that, we can get Widmanstatten structure, but since the grains are grown to a large extent as well as, we are getting a very needle kind of a structure. This overall microstructure does not appear good and then, it generally shows the 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 its particulate regime and then we see certain nucleation of this beta precipitate, which is again BCC in nature. So, we see very fine grain structure with very nicely response beta in that. So, that essentially gives the 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 that gives a very uniformly dispersed microstructure and that is superior and its mechanical property in terms of yield strength and in terms of its fatigue strength.

So, what we can see is that heat ripple is very essential or key component in terms of altering the mechanical properties. So, we can increase the fatigue strength by order of approximately 2 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 very key components because surface is 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, coating should be biocompatible enough.

So, some coatings can also be applied, the ceramic coatings can just also be applied. We can also do certain treatment, chemical treatment to it to the surface of titanium, so that it becomes much more compatible with the body. Then, cells can release, start growing on to them. So, that is also one more key feature of utilizing titanium implants that we can make use of the titanium oxide, which grows on the surface and then make it a chemical reactor and then, also treat it thermally, so we can achieve a very good biocompatible surface out there. We also realize that the aluminum tends to decrease the passivation reason, 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 and titanium 6 aluminum 4 vanadium alloys is. So, basically I end my lecture here. Thanks a lot.