Introduction to Biomaterials

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Module No. # 01

Lecture No. # 28

Biocompatibility of plasma Sprayed Carbon Nanotube Reinforced Hydroxyapatite Bioceramic Coating

In this lecture, we learn about the Biocompatibility of Plasma Spread Carbon Nanotube Reinforced Hydroxyapatite Bioceramic Coating. From this particular case, we are utilizing hydroxyapatite, which is a bioceramic material with some certain reinforcement of carbon nanotube, perform a superior material with a with a biocompatible nature; and this particular material has been synthesized using plasma spraying to form it as a coating. From this particular lecture, we have seen hydroxyapatite, which is being reinforced with carbon nanotube, I since it is a biocompatibility… We are just going to check its biocompatibility, and this material has been sprayed - plasma sprayed to form a coating on to an implant material, because we realize that certain biometallic implants, implant material, they do not have good wear resistance, at the same time, they sometimes underperform as a good compatible material with the surrounding tissues that is the reason, there is a need for producing a coating on to a implant surface so that the overall performance of the implant can be enhanced.

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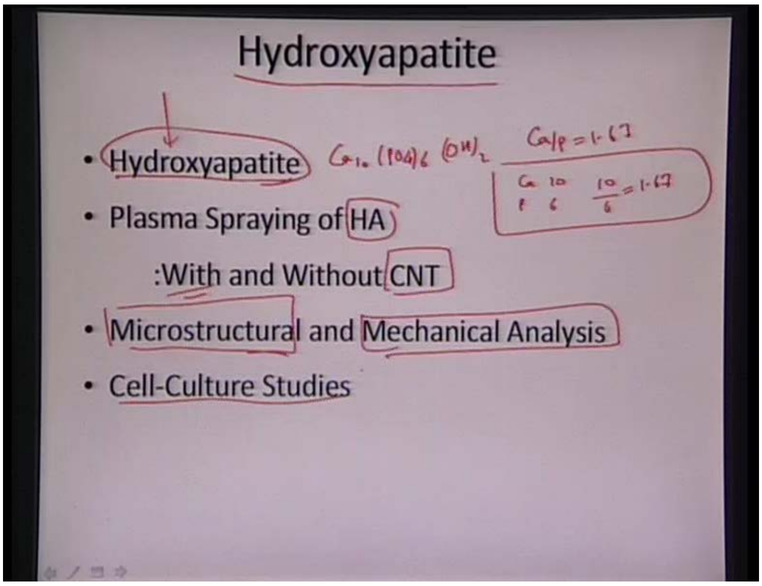

Hydroxyapatite

- Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$
- Plasma Spraying of HA
  :With and Without CNT
- Microstructural and Mechanical Analysis
- Cell-Culture Studies

$Ca/P = 1.67$

$Ca\ 10$ $\frac{10}{6} = 1.67$
$P\ 6$

So hydroxyapatite has been well known for as a very important material, it is described see it a PO 4 whole 6 OH twice; so it is a apatite structure, which is a calcium bar phosphate ratios similar that of bone, which is a approximately 1.667. So that hydroxyapatite is well known biocompatible material with Ca by P ratio of 1.67; and now this material has been plasma sprayed with and without the carbon nanotube, this is denoted by C CNT. Hydroxyapatite is a well known bioceramic; hydroxyapatite the chemical composition of hydroxypatite given as Ca 10 PO 4 6 OH twice. So hydroxyapatite is a well known bioceramic with a calcium of phosphate ratio of 1.67 as we see the Ca is around 10, P is around 6, so 10 by 6 it becomes around 1.67.

So this particular C by P ratio is similar that of which is found in the bone mineral, which is apatite, similar to that of the apatite, it is also 1.67. So we see that hydroxyapatite is the ceramic part, which is available with the collagen, and then it though therefore, hydroxyapatite is consider as the ceramic, bioceramic material, which more compatible with the body itself. And then this hydroxyapatite HA is being plasma spread with and without carbon nanotubes, I mean carbon nanoubes is denoted by CNT, and consequently I will see it more of the micro structural in a mechanical analysis of how how and what this CNTs are contributing, followed by the cell-culture studies in order to say whether hydroxyapatite is getting compatible, once we are adding carbon Nanotube as a reinforcement.

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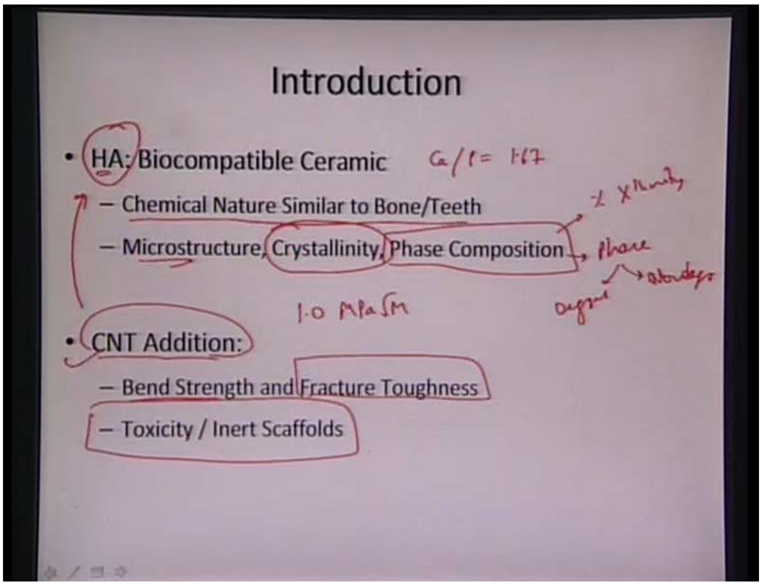

Introduction

- HA: Biocompatible Ceramic
  - Chemical Nature Similar to Bone/Teeth
  - Microstructure, Crystallinity, Phase Composition
- CNT Addition:
  - Bend Strength and Fracture Toughness
  - Toxicity / Inert Scaffolds

Ca/P = 1.67

% X'llinity

phase

degrade

[illegible]

1.0 MPa√m

So we know that hydroxyapatite is a biocompatible ceramic, with as we saw that C by P ratio is 1.67; and this bioceramic, it has chemical nature, it is very similar that of a bone and the teeth material, so that forms the mineral part of our bone and teeth, that is nothing but apatite. And coming to it, the microstructure can also very dominating effect, the kind of crystallinity of hydroxyapatite can also alternate properties, also the kind of phase, which are being generated after the processing can also impart very different properties to the hydroxyapatite; it can also lead to some degradation of phase, it the percent of crystallinity, also the kind of phases, which have been generated; those process can be degradable; those can be non degradable.

So we need a proper proper combination of those phase compositions in the hydroxyapatite, even after processing. And but the basic problem with hydroxyapatite, it is a ceramic and therefore, it is very brittle; it is fracture toughness is to the order 1 mega pascal root meter, which is very poor. So, we often see that the ceramic once you drop it, it basically breaks; so we take a ceramic, hydroxyapatite, we tend to drop it, it will basically break. So to enhance such mechanical properties, so enhance its fracture toughness, we tend to it carbon nanotube. So we add carbon nanotube in order to increase its bend strength, and the fracture toughness; so fracture toughness is a key part in terms of its adding the reinforcement of carbon nanotube.

But again in carbon nanotube, it is said it there was (( )) full of thoughts that carbon nanotube is nothing but graphitic layer, graphitic sheet, which has been rolled as a tube, and the diameter of this tube is to the order of couple of nanometers. So the two school of thoughts, one one group says other than nano is deleterious to body, because it can penetrate through cell walls, it can get accumulated somewhere, and then it is highly deleterious for the body, because we cannot take it out, we cannot even seat so nicely, so how will you how will you take it out, and we will just get logged into some location of the body, so it can induce some toxic effects.

But the second school of thought basically it comes out from from the from the truth that carbon is the basic form of life; so why anything called, which is carbon in nature like graphite, where it should be deleterious to the body. So there are two counter arguments, which are so much nice, which are very highly reported in the literature that carbon nanotube, it is toxic, and it is non-toxic. But people have people do have seen some effects of irritation or toxicity whereas, other group also has seen apatite precipitation on to the carbon nanotube surface, so there is so these where to carefully view these two particular aspects, before we relate to take them for clinical trials. So ideally, we are adding carbon nanotube as a reinforcement in the hydroxyapatite to include fracture toughness, we also need to confirm whether these scaffolds will be toxic or will be cytocompatible, so we need to take that part also in consideration.

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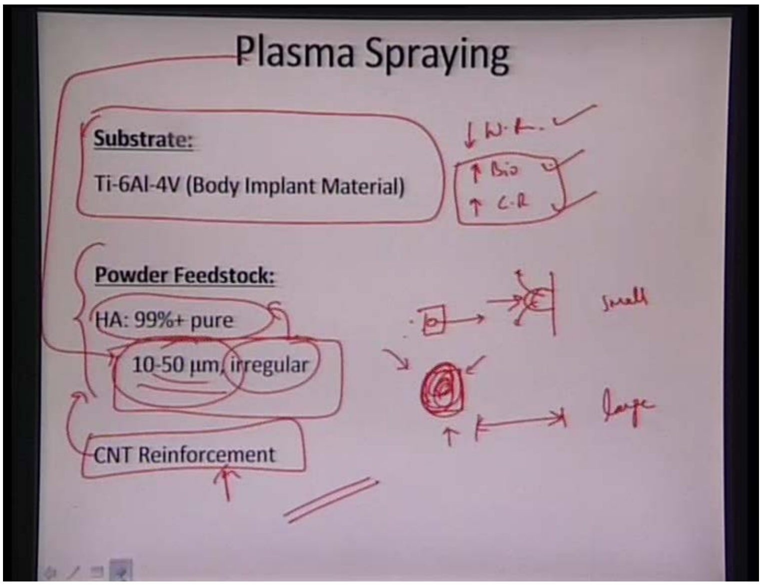

Plasma Spraying

Substrate:

Ti-6Al-4V (Body Implant Material)

Powder Feedstock:

HA: 99%+ pure

10-50 µm, irregular

CNT Reinforcement

An ideally this coatings are done on the bioimplant material, because we realize that the Titanium-6Aluminum-4Vanadium implant they are they have very poor wear resistance, also the so the also we phase ceramic coating on to it, we can increase its biocompatibility, we can also increase its corrosion resistance. So we can see that by inducing certain coating to it, by providing certain coating to it, we can improve its mechanical properties, so we can improve its wear resistance, we can improve its chemical properties, we can improve its biological properties, so that is the overall concept behind performing a coating on to the implant material.

And in the plasma spraying, we utilize a hydroxyapatite powder, which are more than 99 percent pure and plasma spraying requires that we have powders which are approximately 10 to 50 micrometers in diameter, which can be irregular or spherical in shape that is in metal; but ideally it should be 10 to 50 micrometers in diameter. If they are very fine particles, then we will not able to overcome the (( )), let because therefore, particle is flowing, it needs to overcome a certain shock, if something is getting impacted on to a substrate, so there will be a (( )), and the particle has to overcome the particle shock, so they have to be of a particular size. But at the on the other hand, if they are very huge in size, the surface will not meld at all, because the all the heat will be utilize in melting a surface, but that heat will not be sufficient to melt the particle, because it has to cover very short distance in very short time.

So the particle will not saying the pure full for longer time, so larger particles also face a problem, and smaller particle also face a problem, so that is a reason. A ideal range is around 10 to 50 micrometer of diameter, so that particular of powder particle has to be utilized in terms of plasma spraying, followed by it that will also need to disperse the carbon nanotube; because carbon nanotube is a very fine fine particle, like fine tube tubular structure; so because of it is a very high surface either tend to be very, very unstable, and then the tend to agglomerate with one another, that is the overall thing behind it. So we need to disperse some of this carbon nanotube, and disperse them in the hydroxyapatite matrix, so that we can utilize the CNT - individual CNT in terms of taking the the basically extracting the superior mechanical properties.

CNTs have a elastic modulus to the order of 1, 1.4 tera pascals and (( )) the order of giga pascals. So, that pattern will not utilize in terms of basically adding them as a reinforcement, and then once you have there was a reinforcement, then we can achieve a overall very good implant with the very superior coating, and the overall performance of the implant will go drastically high.

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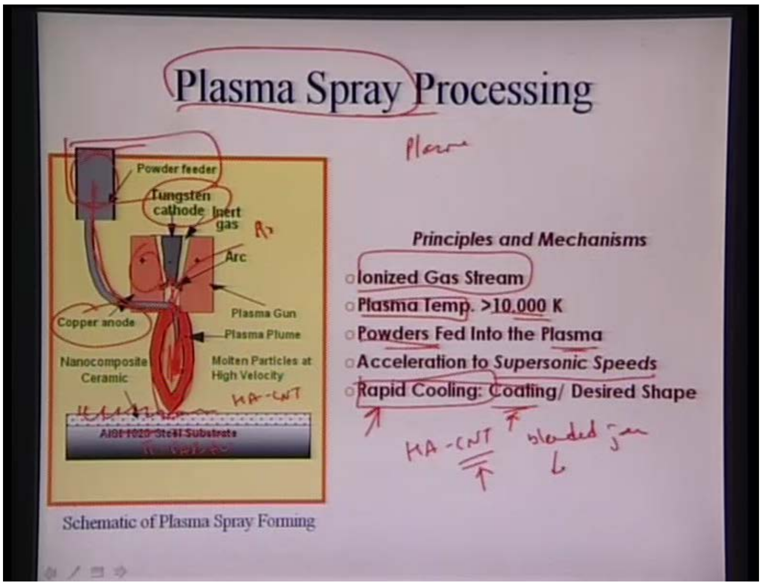

Plasma Spray Processing

Schematic of Plasma Spray Forming

Plasma

Principles and Mechanisms

- ○ Ionized Gas Stream
- ○ Plasma Temp. >10,000 K
- ○ Powders Fed Into the Plasma
- ○ Acceleration to *Supersonic Speeds*
- ○ Rapid Cooling: Coating/ Desired Shape

HA-CNT

Plasma Spraying: How does… Plasma is nothing but a plasma is ionized gas, so we see, we have ionized gas that is being struck as an arc between the tungsten cathode and the copper anode; so we strike an arc between the tungsten cathode; tungsten cathode and the copper anode, which is out here, so we see the copper anode out here. So an arc is struck between them; and that arc basically leads to generation of plasma, because we supply a gas, which can be organ and that organ passes through this particular arc, and it gets excited to generate the plasma, so we see the plasma out here.

And then we feed the particle, so we are we are we feed the particle powder particles through this one, and we inserted in the plasma plume, and we accelerate this particles via some carrier gas. So we have plasma temperature and excess of 10000 kelvin, and we are fitting this powders into the plasma, and we are accelerating this particular powders to supersonic speed via some carrier gases, and once it impact on to this particular surface, in this case we have Titanium-6Aluminum-4Vanadium substrate. So in this particular case, we have Titanium-6Aluminum-4Vanadium substrate, and then we basically we are basically deposits in this particular ceramic coating, this hydroxyapatite CNT.

And have ideally this powders HA-CNT powders are being blended, they have been boiled milt, they were (( )), blended in (( )), and then we are seeing that this CNT powder CNT excess getting (( )) out by itself so that is the overall deal with it that the plasma is the ionized gas, through which we basically feed the powders in the plasma plume, and then accelerate to supersonic speeds, it is move like playing with the water balloons. So we are taking a water balloon, and then we are impacting it on to a on to a surface; so there is a kind of a layer by layer deposition, which really occurs, via this particular processing.

So we take we have powder particle, it is accelerated via… Accelerated, because of the carrier gas, it is taking it, and then it passes through the plasma, surface gets melted and a particle becomes more molten or single molten in nature; then once it is impacting a substrate it forms a splat. Unless and then consequently or successfully another splats, another molten as molten power particles, they gets impacting on to the substrate, and from that we develop the coating. So that is how we see a deposition technique is being utilized in terms of creating a gridded kind of a structure out here. So we that once it is impacting on to substitute and it undergoes rapid cooling and that forms a coating on the Titanium-6Aluminum-4Vanadium substrate.

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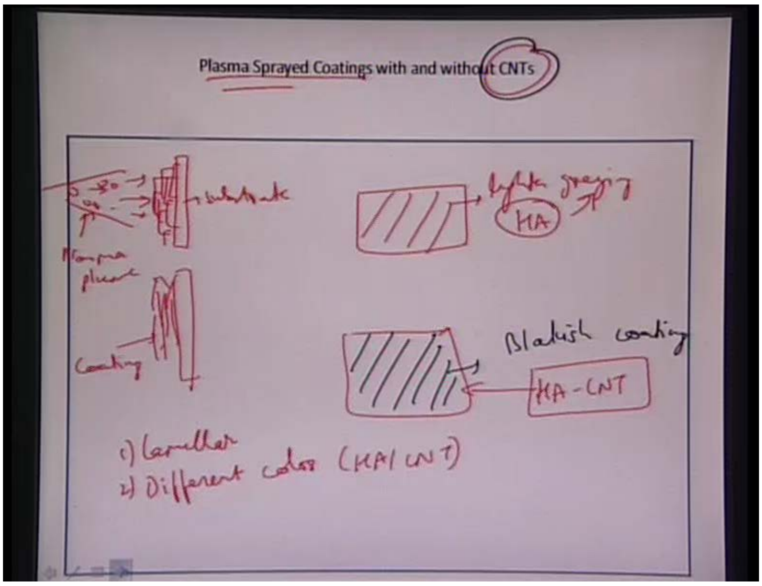

Plasma Sprayed Coatings with and without CNTs

So, ideally the coating looks more like this; we have a molten or semi molten particle, then it basically goes on to on to impacting the particular substrate, and it splashes out like this, and we have successful deposition will lead to formation of coating. So coating looks more like more like laminar in structures, so we have laminas; and then we have this particular substrate, this is a substrate and and we see the coating, which his being deposit deposited like this; this is coating. So this is what we are seeing that we have a stream of powder particles, which keeps impacting on to the substrate, and then we have all the molten, semi molten particles, this is the plasma plume plasma plume and up on impact on to the substitute, it forms a coatings. And coating with and without CNT, ideally, the hydroxyapatite is more whitish or grayish in nature, so the overall field of this particular coating will be much more lighter or the grayish light, lighter grayish in nature.

But once we had carbon nanotube, carbon nanotubes are much more blackish in nature, and what we see is that we are achieving totally, a total kind of a black coating, so we see totally blackish coating, once we are… Blackish coating will be appearing, once we add carbon nanotube into the particular materials; so that is what is being observed for the plasma spread coatings that first of all they form a lamellar structure lamellar structure; and then coating is much more… There is much more difference in color, because of the narrate nature of the hydroxyapatite; of hydroxyapatite and CNTs and that is what hydroxyapatite coatings appear much more grayish or light light half white in color HA plus CNT coating will appear much more blackish in color, because of the CNT contained in out there, that is the overall thing which we see out here.

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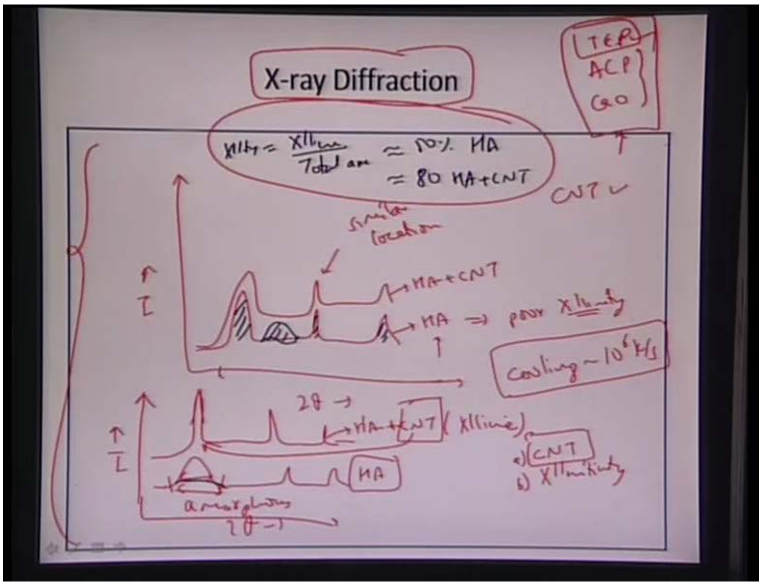

X-ray Diffraction

And again the X-ray diffraction will also come out to be it will show the all the peaks of our hydroxyapatite, it a certain peaks of hydroxyapatite, we will see certain peaks of hydroxyapatite, but at the same time for the hydroxyapatite facing something like this. Since CNT content is so small, and the hydroxyapatite peaks are much more stronger, we will see approximately similar coating, with similar kind of peak, this is 2 theta, this is the intensity. We will see peaks at similar locations, even for once we have hydroxyapatite with some CNT reinforcement, so we have HA plus CNT, it will show the similar peaks. But the difference will be that hydroxyapatite itself will have poor facilitating, because they do not get much time to… They do not get much heat in terms of in getting in achieving a slower cooling, so they tend to get amorphous, because we because the cooling in the plasma spring is to the order of 10 power 6 kelvins per second, so with such high cooling rates that is very easy that, some amorphous structure can also get generated.

So, ideally, we see some broadening of this particular peak in hydroxyapatite. So, this particular regime out here will you much use in a very huge background that will show very wide, widening of this particular peak at certain location. So, we see too much widening in hydroxyapatite (( )) pattern, whereas once we have carbon nanotube, you see much sharper peaks; we see much sharper peaks for the same locations, this tells - this particular broadening tells that the structure is much more amorphous in nature, much more amorphous in nature with time, where the hydroxyapatite; but this HA plus CNT, it is much more crystalline in nature, so we see 2 theta along this side, intensity along this side, so we see that this particular structure is much more hydroxyapatite, much more amorphous in nature whereas, hydroxyapatite CNT is much more crystalline in nature; and that happens that that that cool it as there is something with respect to CNT; and that is the reason we are seeing much sharper peaks, and the crystallinity part is being dominated by the CNT itself.

So, first of all we can directly say, there is some difference in crystallinity is coming out with the with respect to CNT; as secondly there is there is much more amorphous content in the (( )) unless say that there was some secondary piece which also generate out, so there can be additional peaks as well, there can be tri calcium phosphate, there can be amorphous calcium phosphates, calcium oxide, all these species can also generate will any processing. But in the plasma spraying, there are processes are so rapid, we can just see either TCP faces, which is much more amorphous in nature. So we can see that this particular structure is being dominated by presence of CNT, but CNT is responsible for inducing these crystalline peaks; and secondly there can also be some effect of… in terms of the shaper peaks, they are not - CNT peaks are not really being observed out here.

The second is the crystallinity part is being being dominated by the carbon nanotube content; and if we see that the processing can also induce some different peaks, which can be tri calcium phosphate, amorphous amorphous calcium phosphate, those can even be calcium oxide, but the what we what we are seeing in this particular spectrum is there is no presence of any other secondary peaks, but there can be also presence of certain easily peaks, because of the rapid characters, which is involved in the plasma spring. So we can also observe some TCP peaks that will induce certain amorphous structure or the amorphous nature in the particular coatings.

So ideally, we can see that the facilitative, which is being induced, that can be calculated by the area under that particular peaks, so we can so we can see that, but the area under particular peak can provide us the overall content of this particular… Or the crystalline nature of this particular peak; and we can also see that the… And if you take the peaks which are much more amorphous, so we can see that we broadening of the peak, so the amorphous nature can also be deducted from there.

And we can find the crystallinity is only the crystalline peaks total by the divided by the total area; and that area comes out to be around 50 percent for only have whereas, it comes around more than 80 percent. So we can see that this particular values are around more than 80 percent for hydroxyapatite plus CNT; so that tells that clearly CNT is playing a part in terms of increasing the increasing the crystallinity of this particular structure, so that is what is so critical about this part is that CNT serve as certain sites for supplying some additional heat to the hydroxyapatite; and then making it much more crystalline.

So in letting it crystallize for a longer duration of time, because once the plasma spraying is being done the whole powders stays in the plasma plume for couple of micro seconds; and that time is not sufficient for the hydroxyapatite, (( )) it go undergo very rapid cooling to the order of 10 to the power 6 kelvins per second, so they do not have enough time to get crystallize again, once they heated to very high temperature, that tend to be get amorphous, and then once it is nothing but liquid or solid semi-solid state, I want to cool so rapidly, it does not get time to crystallite itself.

So, somehow CNT is a playing a part in supplying that additional heat, and letting it stay hotter for longer time, and that is the allowing to reduce the cooling rate, and then achieve much more crystaillinity of the hydroxyapatite in presence of carbon nanotube. And at the same time, you do not see any CNT piece in the X-ray diffraction, because the overall hydroxyapatite peaks are much more dominating. And depending on the concentration of CNT, they may not just appear, so that is the overall deal with the X-ray diffraction. Secondly, we can also see that secondary phases such as tri calcium phosphate, amorphous calcium phosphate, calcium oxides or even titanium oxide can also get generated out here, depending on how much surface itself is also getting oxidized or getting exposed to high temperature.

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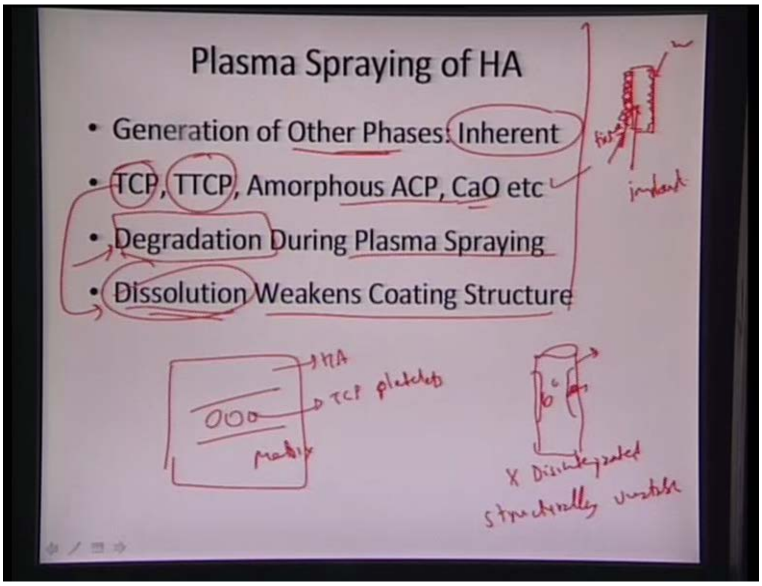

Plasma Spraying of HA

- Generation of Other Phases: Inherent
- TCP, TTCP, Amorphous ACP, CaO etc
- Degradation During Plasma Spraying
- Dissolution Weakens Coating Structure

So, generation of secondary phases or the other phases becomes inherent. So we can see tri calcium phosphate, tetra calcium phosphate, amorphous calcium phosphate, calcium oxide etcetera, which can also get generated during the processing. And again if you are seeing all those phases, it is nothing but the degradation of this particular coating, to that degradation should not happen during the plasma spraying. And again once we have this particular degradation, it will determine the mechanical properties of the coating. And again if we start having certain bio observable or the amorphous phases, they will dissolute time, and then that will become the coating structure.

So, we can see if we have certain certain structure, it can from may be like platelets kind of structure you can form within the matrix, so if we have some hydroxyapatite matrix, we can see formation of tricalcium phosphate as platelets. I will again if you doing making some reinforcing structure such as an implant; and if we start seeing with this sites are getting loose and up or they bend or they some structure we are losing certain material at certain locations, this is basically not good, because of is getting disintegrated, again structurally unstable. So that thing should not happen, so that is the reason want to maintain or control the dissolution of this particular implant.

So we need to very control degradation of the material, so in even when we want degradation, it should be much more controlled in nature, because if you want the bone to take, bone to fill up the particular material, the material should start degrading from a surface, and then bone should take take place of that particular dissolved surface in in in order to achieve good bonding with the implant, and the surrounding tissue. So, this is the tissue, which can basically replace the surface, and then basically take the place of the implant; so you have to want the degradation, you want to have a very controlled degradation, and if we have some secondary phases, which have been generated into the material, during processing that is not good; so that will make the structure highly unstable, and we cannot utilize that as the weak coating structure onto the implant material.

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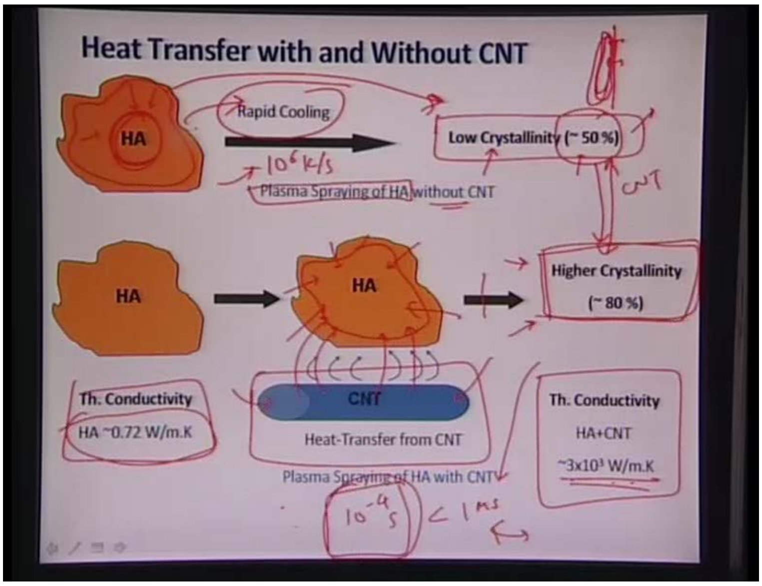

Heat Transfer with and Without CNT

HA

Rapid Cooling

10^6 K/s

Plasma Spraying of HA without CNT

Low Crystallinity (~ 50 %)

CNT

HA

HA

Higher Crystallinity (~ 80 %)

Th. Conductivity

HA ~0.72 W/m.K

CNT

Heat-Transfer from CNT

Plasma Spraying of HA with CNT

Th. Conductivity

HA+CNT

~3×10^3 W/m.K

10^{-4} s < 1 ms

So what is happening in presence of CNT? First of all, we have a hydroxyapatite crystal, which is basically molten, and then it impact on to the substrate, it undergoes a rapid cooling, because cooling in the plasma sprayings into the order of 10 to power of 6 kelvins per second. And then in absence of CNT, basically hydroxypatite does not have enough time, because of its lower its lower thermal conductivity is to the order of a 0.7 to watts per meter meter kelvin; it is not able to generate enough heat in itself, so that it can pass it on to the center or so that it can collect the heat at the center or the core of it.

So obviously always surface gets heated up, always surface get heated up, and then it will basically cool down, once its impact with this with the substrate, and it achieves the very low facility, because once you have impact on those substrate, it is forming a thin splat, its thickness is very, very fine, and so most of the surface is basically basically divide of the heat, so just heat is being released to the substrate very quickly. So, it is not finding enough time to heat up itself, at the same time it gets release very quickly in absence of any CNT.

But in case of CNT, what happens; but CNTs they observe very high heat, because the thermal conductivity is to the order of 3 orders of magnitude higher than that of a hydroxyapatite, if apatite are 1 watt for meter Kelvin, hydroxypatite where CNT will have thermal conductivity order of 3 orders of magnitudes higher; 3000 watts per meter kelvin. So what happens? During heating process, CNT will observe most of the heat;

once CNT is observe most of the heat, it will acquire enough heat that it can transfer it back to the hydroxyapatite; once it is even when impact on to the substrate.

So, now hydroxyapatite once it is impact on to the substrate, it will start getting heat from the CNT; and now it will get enough time to get crystallized, because now some heat is being applied supplied to it from CNT. So CNT is keep giving heat to it, and then it basically achieves very high crystallinity; so that is that is the difference once we have see hydroxyapatite with and without CNT. In case of without CNT, it basically undergoes very rapid cooling, rapid the order of 10 power 6 kelvins per second, and it induces very low crystalinity into material.

But once we have carbon nanotube in presence in near to the hydroxyapatite splats, because of the higher thermal conductivity of CNT is which is to the order of around 3000 watts per meter kelvin, it captures much more rate while it is in the plasma plume; so once it has very high heat available to itself, so while cooling, it can impact the same heat back to the hydroxyapatite splat, and that heat can be captured by hydroxyapatite splat to basically start precipitating itself again, as a crystalline material.

So that amorphous part is basically again lost, because it is now undergoing a lesser cooling rate; a cooling rate is not as drastic as it was in absence of CNT, now because of CNT, the overall cooling rates have been decreased, because CNT itself has so much heat, that it keeps giving it to the hydroxyapatite surface, and that releases that release heat basically is being captured by hydroxyapatite to induce vicinity in the hydroxyapatite, and we can achieve higher vicinity, which is to order of around 80 percent. So we can see this difference that CNT is inducing this crystalline effect and increases increases it from around 50 percent to approximately 80 percent, and this is all happening during the plasma spraying of hydroxyapatite.

So the duration time is less than a microsecond or a approximately few microseconds or less than a may be little a couple of microseconds or less than a millisecond and the the duration time is around 10 to the power 4 it is around… The dual time of this particular particle in the plasma plume is around 10 power minus 4 seconds, so it is less than a millisecond, so that is the duration of time we are talking about out here, that that time should be sufficient for the CNT to capture the heat, and release it back to the hydroxyapatite in a certain longer for certain longer duration.

So this time is only available for hydroxyapatite to either absorb heat during the plasma plume, and once it is basically settled on to the substrate, it does not have any heat left in itself, because all the heat is being lock to the substrate, whereas in presence of CNT, this time is the approximately sufficient for itself to get heat to absorb enough heat, and then once it is impacted on those substrate, it can release that particular heat back to the hydroxyapatite crystal and therefore, the overall crystallity can be increased drastically high; and the overall idea behind increasing the distillity of hydroxyapatite is that we achieve a stable structure, which does not does not degrade with time abruptly.

So if we have certain phases - different phases which are being evolved; so, those once we start degrading, they will weaken the overall structural integrity of the whole implant; so in this case, we can get a much more control over the structural implant that though we know that the structure will not degrade with time, and we can design accordingly.

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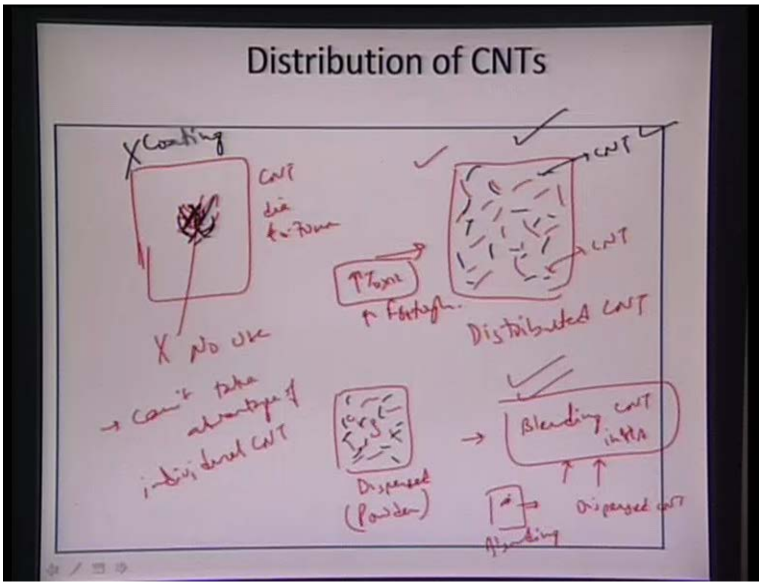

Distribution of CNTs

And again the the CNT is they have to be distributed. So if we are seeing a particular structure, we have hydroxyapatite, and we have seen which are all agglomerated; so CNT is a nothing but diameter of around 40 to 70 nanometer for the for the double volt, for the multi volt CNT, and if they are agglomerated, it makes no use, because they are all agglomerated, and we cannot take advantage of single nanotubes of individual nanotubes. So that that will that will create a problem, because once we are not able to capture the advantage of single nanotube that does not make sense, so we need to have a structure, which has much more distributed CNT; so we had CNTs throughout the matrix that will give out much better properties. So all CNTs distributed, distributed CNTs will give out much enhance mechanical properties. So that is what we are really looking for.

And owing to the very a high surface area of carbon nanotube, they tend to basically agglomerate; so that agglomeration has to be avoided in the first stage itself, that is the blending of powder. So so if you utilizing a powder which is the which serves as the heat stroke of plasma spraying if you want to avoid the agglomeration that has to be avoided in the blending stage itself that we are take powders, and then we take powders of hydroxyapatite, and then we mixed with CNT. So CNT is basically should get dispersed in the powder formation itself; so in the powder (( )) of itself, we should have dispersed CNTs in the matrix. So we should have CNTs which we we should have dispersed out here in the powder stage itself, and they should not get agglomerate later on in the coatings that we have all the CNTs, which are all entangle in the coating that is not good, so that is not good. But once we have CNTs, which are all distributed in the matrix like here, here, here; if you have CNTs which are distributed throughout the matrix that will be very, very good.

So to so to do that we need to have a CNT disperse much at the ball milling - the milling the blending stage itself that we once we are blending it, we need to disperse the CNT in the hydroxyapatite matrix. So if we if we are able to achieve this particular blending in hydroxyapatite itself; that same particular phenomena we are thinking that it will get retained even of the plasma spraying. So this thing becomes highly essential that we are able to disperse the carbon nanotube in hydroxyapatite matrix at the stage of blending itself.

It you are not able to achieve this particular blending and dispersion of CNT during blending, then the agglomeration of CNT will remain even during this plasma spraying process; so once we are blending it, we should be able to have disperse CNT, otherwise otherwise this particular agglomerated CNTs will remain even at the… They will remain even at the plasma spraying level. So we need to avoid this particular structure that we should not get agglomerated CNTs even in the blending stage.

But only problem with this distribution of CNT is at this particular structure is good, so we need to so we have CNTs are there on the surface of the particular hydroxyapatite surface, it can also induce certain toxic effect as well on the surface. So we need to also to take care whether these are CNTs are forming a toxic surface or not; same time we need to see the dispersion is increasing the fracture toughness part or not. So those all all are all are the essential components to discuss whether we want to have CNTs distributed, and then we are able to achieve toughening from it.

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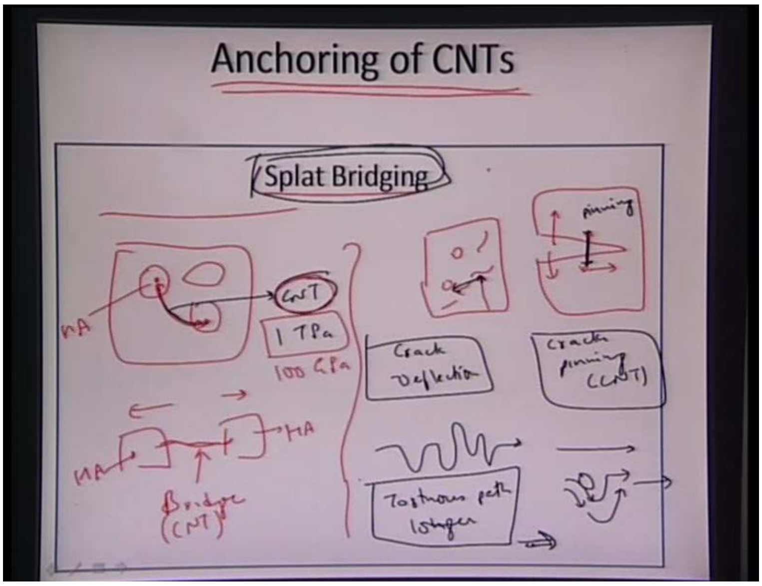

Anchoring of CNTs

Splat Bridging

So CNTs once they are distributed, they can provide very nice anchoring; they can provide a splat bridging, it means in the structure plasma spraying structure, once we have fracturing the particular material, we will have one splat like this, one splat like this, spalts like this; they can get anchored by the CNT surface. So, if we have a CNT surface, we can see this particular anchoring, which is being done by the CNT, so we have CNT like this, so because of their exceptional mechanical properties, which are because CNT is a modulus of around more than one terapascals, and fracture strength of around hundreds of hundred around hundred gigapascals.

So CNTs can be very strong in terms of reinforced in this hydroxyapatite splats; so if we had this particular hydroxyapatite splats, so this was hydroxyapatite, and all this is CNT, so we can CNT is forming a (( )) bridge between the two; it will encourage these two locations, and once this splats are getting separated far apart, it will form a bridge. So we have achieved hydroxyapatite, we again have hydroxyapatite, and once you applying certain force to separate them, CNT will act as the bridge. So we have CNT bridge that will basically induce much more toughening to the particular material, because the the modulus also is very high for CNT, and fracture strength is also approximately 100 gigapascals for the CNTs, so that that particular toughening is being given by the CNT.

Additionally, CNTs can also serve as the crack deflection part; so if we had CNT somewhere, if we had some CNT somewhere, then if crack is really flowing, once it encounters the CNT, it will get deflected, because of its higher mechanical properties CNTs would not allow the cell the crack to proceeds further. Additionally, they can also provide certain reinforcements, if the crack is propagating like this, and we have CNT, which is approximately like this; then this particular part cannot grow grow further it can get separated further, because we have CNT out here in this particular regime to take care of the… If you have CNT out here, then it basically bridging the… Or pinning down the crack. So crack pinning can also be assisted by the CNT, so that part also can be taken care by the CNT; so we have splat bridging, we have crack pinning, we can also have something called crack deflection.

So once once a crack is really flowing or propagating, then it can encounter the CNT, and then it can get the splat time. So CNT surface also help in deflecting the crack, so eventually crack has to take a longer path; once it has to go from one end to another end, it has to take a much more tortuous - tortuous path and longer path; so that basically again makes the crack to flow very with much more difficulty, because you had a crack bin propagating straight, it is not facing any obstacle, but as soon as an interaction of the CNT, it has to become flow in another direction.

So, now it is very difficult for the crack to come back to this particular stress state; now much more energy is being absorbed in terms of deflecting the crack, and then making the crack come back to its original line of propagation. So, it is inducing basically much more… It is inducing much more energy it is requiring much more energy in terms of propagating the crack, and so that is the reason how CNTs can improve the fracture toughness via splat bridging via pinning the crack also via crack deflection and providing a contour or a tortuous longer path to the crack. So this this are all the mechanism, by which a CNTs can anchor the CNTs can anchor the hydroxyapatite splats. First by a splat bridging that it can bridge this splats, it can anchor act as a as an anchor; secondly it can also provide crack deflection, it can also serve as crack pinning pinning location, it can also provide much more tortuous nature to the crack via its deflection. So, now crack has to take much more contour path to come back to its original location, and then propagate further. So these are all the mechanisms of toughening via carbon nanotubes.

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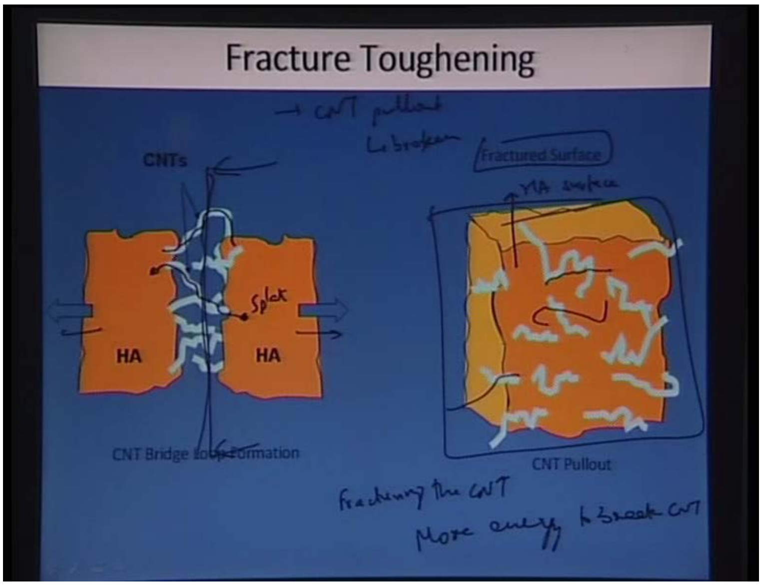

Fracture Toughening

So if we see it more like this that we have hydroxyapatite splat, so we have splat out here; and then CNTs are basically bridging the two slats via forming certain anchors. So we have one anchor out here, one anchor out here; and once we apply supply enough force to it, so that it basically fractures at this particular location, the top position looks more like this. So we are seeing this particular phase like this, so we see that there are some CNTs which are pulled out. So CNT pull out it means that we are fracturing the CNT, we are fracturing the CNT; and since CNT have such high strength, basically now more energy is required to break them. So therefore, now material absorbs much more energy to break the CNT. So we are achieving fracture toughening via the various methods such as crack bridging splat splat bridging, pinning the cracks and also providing a contour tortuous path, additionally we can also achieve it by CNT pull out.

So, we are seeing that CNTs have not to be broken, so that a material can fracture itself; so that is what we are seeing out here that CNTs will basically being pull out from a surface; so we had etched surface, hydroxyapatite surface, which has been fractured; so we have fractured surface and we can see CNT, which are being which are coming out as a pullout from the particular surface to impart much more toughening to the hydroxyapatite crystal.

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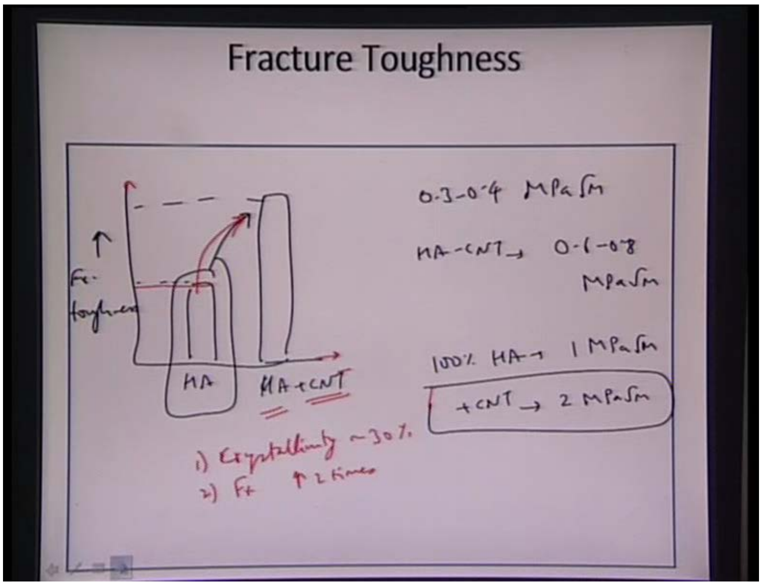

Fracture Toughness

So the fracture toughness becomes a particular way of evaluating the mechanical property of hydroxyapatite. So, we see that once we have hydroxyapatite only, it will show certain level of fracture toughness; if you take a fracture toughness of only hydroxyapatite, I will show certain value; and with the addition of addition of CNT, it goes to approximately double. So we had a hydroxyapatite plus some CNT is approximately 4 to… 4 weight percent carbon nanotube that will approximately double the fracture toughness. And since this coatings are very, very porous, the fracture toughness of this hydroxyapatite coating can be to the order of around 0.3 to 0.4 megapascal root meter; because we need also this coatings to be very porous to assess with the biological compatibility so that cells can grow on to it; and with HA plus CNT, it can grow as highest around 0.6 to 0.8 megapascal root meter.

But ideally people are seen, ideally it has been absorbed that 100 percent dense hydroxyapatite, hydroxyapatite can be… It can have fracture toughness as highest one megapascal root meter, it is also been proposed in literature that if once we start adding carbon nanotube to it, it can increase the fracture toughness of (( )) 2 megapascal root meter. So that is values we are approximately talking about that how CNTs can provide reinforcement in… Reinforcement, and then it can enhance its mechanical properties via that much order of magnitude.

So if we had hydroxyapatite at certain location, fracture toughness, it can double approximately it can double with the addition carbon nanotube into the hydroxyapatite matrix. So we have hydroxyapatite matrix plus CNT it can improve the fracture toughness via approximately two times. So that is what we are seeing that CNT is increasing the crystallinity, so we are seeing that crystallinity can also be increased by addition of CNT by approximately 30 times - 30 percent times, 30 percent increase, secondly the fracture toughness can also increase by approximately around 2 times, so that is what we are able to see with the addition of carbon nanotube.

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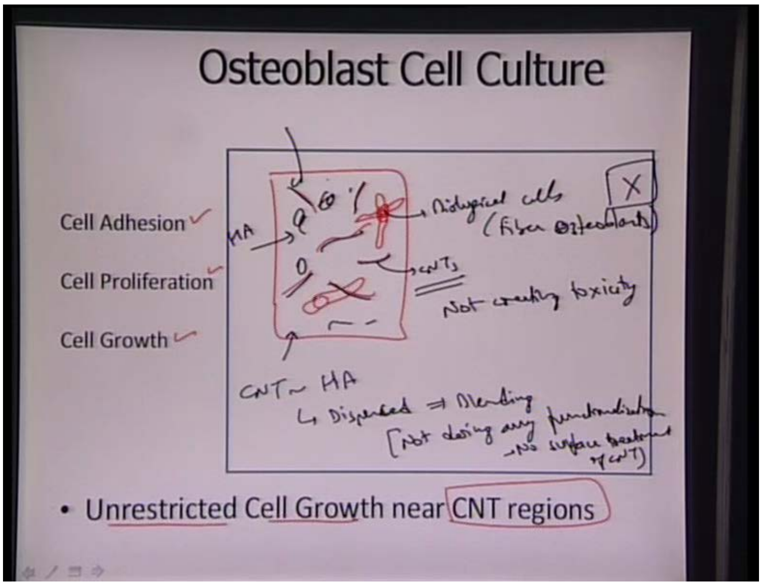

Osteoblast Cell Culture

Cell Adhesion ✓

Cell Proliferation ✓

Cell Growth ✓

- Unrestricted Cell Growth near CNT regions

And coming to the cytocompatability of this particular material, they are three categories to it that cell should be able to adhere itself on to the surface, and then cell should be able to proliferate, and should cell should also grow itself. So, we are seeing this unrestricted cell growth, even near the CNT regions. So we have particular regimes, where we are seeing some CNTs which are growing out here, and over that what is happening, we are seeing that cells are basically was even, when we are CNTs out there cells are able to grow. So we are seeing the cells it is able to proliferate or grow itself more like a fibrous structure, so it is basically growing even over the CNT surface.

So we are seeing that even once we have some CNTs over here, so if we had those all CNTs, and all this has biological cells, it is a nothing but fiber osteoblast. These cells are growing without any hindrance, so that means, that CNTs are not creating toxicity;

otherwise had they been had they been toxic, then we will not see any fiber osteoblast growing on on to the hydroxyapatite surface. So, majorly we have hydroxyapatite matrix, which some CNTs out here and there which are scattered throughout and on the matrix; and the it also appear that CNTs are getting distributed even in the powder stage, it appears at they have some sort of a chemical affinity with the hydroxyapatite matrix itself.

So, CNTs they they appear to have some sort of a affinity for the hydroxyapatite matrix itself, so they tend to basically disperse even just by just by blending, and it means that we are not doing any functionalization; we are not doing any functionalization or surface treatment, no surface treatment has been done on the CNT surface, so we… When we are doing any functionalization, no surface treatment of CNT, still they getting disperse into the hydroxyapatite matrix without any hindrance. So they are getting distributed uniformly on the hydroxyapatite surface without any functionalization; that is the reason they they tend… It appears at they had some sort of chemical affinity with hydroxyapatite surface, and that is the reason they are distributed full uniformly even after plasma spraying, and they are able to enhance the fracture toughness by approximately two times and to come to to come back to the biocompatibility part to come back to the biocompatibility part, we are able to see that this all this osteoblasts are growing on the hydroxyapatite surface, which even have CNT without any hindrance.

So it means that the overall composite is not toxic; so therefore, this overall material is showing superior mechanical properties while rendering some biocompatible biocompatible nature to the implant surface. So, that means that but this material particular material has so was a superior coating in terms of imparting, superior biological response, while maintaining a very high or much better mechanical properties.

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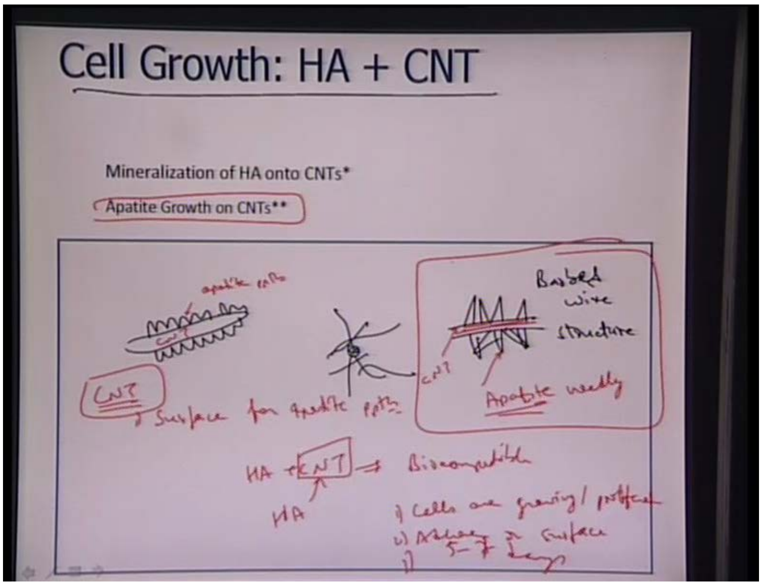

Cell Growth: HA + CNT

Mineralization of HA onto CNTs*

Apatite Growth on CNTs**

So, what we are seeing in this particular hydroxyapatite plus CNT is that the all the CNTs, they showing some precipitation of apatite mineral on to it; so there is some sort of a barbed like a barbed wire like kind of structure what you use in fences; so we see all the fences, they have wires grown all around them. So similarly, we have… We are seeing that CNTs, they have some sort of a needle shaped kind of structure, which is being grown over the… So they become more like a barbed wire structure barbed wire structure, which is being appear, which is appearing on to the CNT surface, so we see that we have CNT, and then this is a CNT, and then we have some sort of a apatite precipitation.

So we have apatite apa apatite needle, which are growing on to the CNT surface; so it means that CNTs are basically serving as a surface for apatite precipitation. So it means that they cannot be so harmful, they cannot be toxic, because they are inducing apatite formation on the on their surface; we are seeing a CNT with some apatite precipitation on to it surface; we are seeing apatite growth on the CNT surface and similar search has been absorbed by couple of researches, so that that means that CNTs are not so toxic, while they are being embedded into the hydroxyapatite matrix; so HA plus CNT is also serving to be much more biocompatible as compared in comparison to the hydroxyapatite itself.

So, CNT itself is not inducing any toxic effects, because we are seeing that cells are growing and proliferating proliferating, they are able to adhere on to the surface, on the surface; and this they are being retained even after couple of days, so even after 5 to 7 days, around 5 to 7 days also we see that the cells are basically there on the surface; and we are seeing this apatite precipitation on to the CNT surface, which means that CNT itself is not very toxic, and hydroxyapatite CNT is coming on to be a much superior material with enhance mechanical properties, and with enhance biological properties as as well.

So that is what the overall thing comes out to be that hydroxyapatite is the biocompatible material, which has chemical composition of Ca 10 PO 4 whole 6 OH whole twice, and then basically, it has basically very brittle. So we tend to reinforce it with some carbon nanotube, because fracture toughness of hydroxyapatite is very low order of 1 megapascal root meter. So that is the reason that we want to introduce some carbon nanotube into it; so that the overall structure becomes much more superior in terms of mechanical property. But people have already debated about the carbon nanotube being much more toxic sometimes or sometimes very biofriendly depending on how it has been utilized.

So to conform whether they tend to be much more biocompatible in that particular work, all this coatings have been synthesized using plasma spraying; and then we have two composite; one with hydroxyapatite with CNT, and one without CNT; and then we realize that CNTs are also serving as the place for apatite precipitation. So they cannot be really toxic in nature; so we are going to see that the fracture toughness was increasing to the order of approximately double. We also realize that the crystallinities of the hydroxyapatite itself can be enhanced from 50 to 80 percent, and they tend to be much more biocompatible.

So, all this is happening that they show increase in crystanality, they show in increasing fracture toughness, but without loss of biocompatibility, that is the key part of synthesizing hydroxyapatite plus CNT as the biocomposite coating; so that is the overall nature of producing this coatings on the Titanium-6Aluminum-4Vanadium implant surface. So that the overall corrosion resistance can be enhanced, the overall wear resistance of the implant can be enhanced. At the same time, we can also induce increase the implant life, because of its increased fracture toughness and the same time we can also make it much more biocompatible in nature; because we can also render some porosity onto that particular coating; so that cells can come adhere itself, and cling on to this particular surface. So overall we are able to see a very superior coating hydroxyapatite with CNT, bio utilizing plasma spray, it… Plasma spraying in this particular case, so that is the overall theme of generating all this ceramic coatings on a Titanium-6Aluminum-4Vanadium biocompatible, biometallic implants surface; thank you.