Introduction to Biomaterials
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Lecture No. # 29
Biocompatibility of Alumina and Carbon Nanotube reinforced Hydroxyapatite

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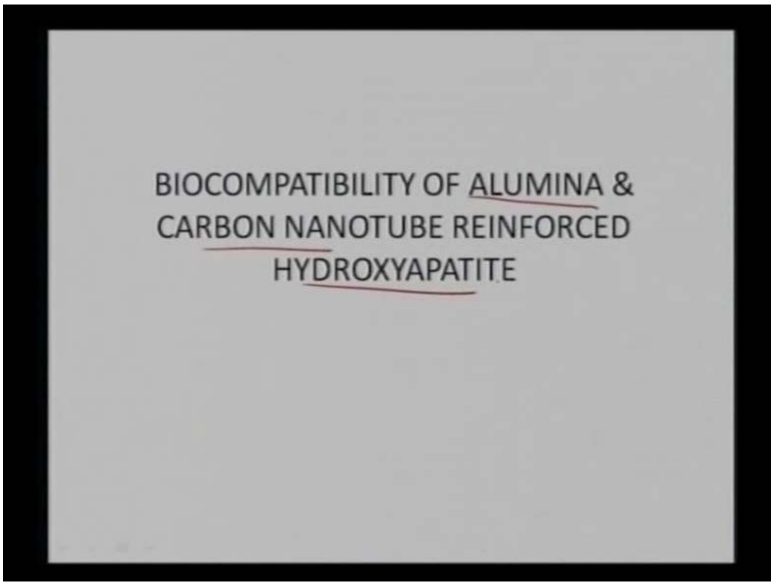

BIOCOMPATIBILITY OF ALUMINA &
CARBON NANOTUBE REINFORCED
HYDROXYAPATITE

In this lecture of we will learn about the biocompatibility of Alumina and Carbon Nanotube reinforced Hydroxyapatite, we also learn the need for reinforcing Alumina, and Carbon Nanotube in a biocompatible Hydroxyapatite. As we have learned in the earlier lectures, that Hydroxyapatite is one of the bioactive materials, so but again the problem is it is highly brittle. So, that is the reason we want to reinforced reinforced with some other materials, such as Nano Alumina or some micro Alumina, and also with Carbon Nanotube in order to see, whether it can support or it can enhance the pressure toughness of brittle Hydroxyapatite.

At the same time we want to maintain at biocompatibility, so we also need to verify that the materialist again biocompatible or cytocompatible, and it is not inducing any toxicity; once it is being implanted into the body. So, in this previous lecture we learn about the biocompatibility, in the need of Alumina and Carbon Nanotube reinforced Hydroxyapatite.

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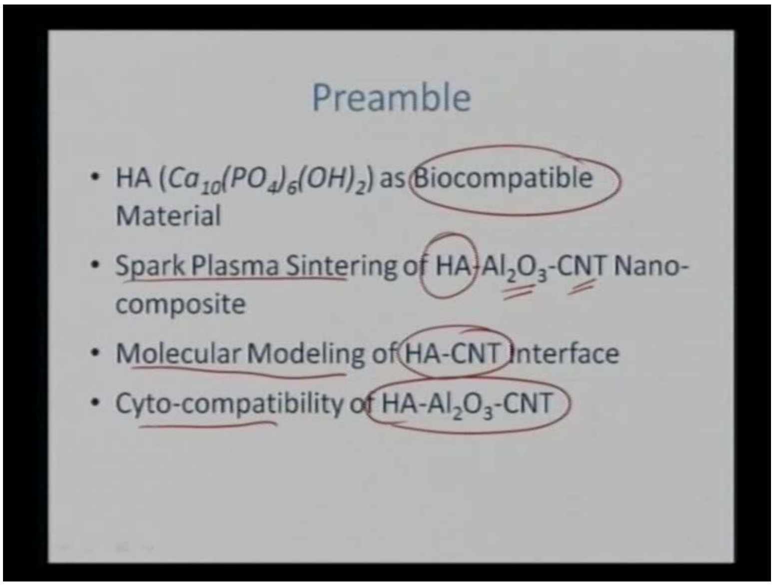

Preamble

- HA ($Ca_{10}(PO_4)_6(OH)_2$) as Biocompatible Material
- Spark Plasma Sintering of HA-Al_2O_3-CNT Nano-composite
- Molecular Modeling of HA-CNT Interface
- Cyto-compatibility of HA-Al_2O_3-CNT

Hydroxyapatite is one of the very well known biocompatible materials, because calcium of phosphate phosphate ratio is 1.67 which is similar to that of bone and teeth, so that is the reason it has been chosen as a (( )) for a biocompatible material, later on this particular material has been spark plasma sintered.

So in this case, we will talk about the processing part; so, this particular material has been sparkled center with reinforcements of aluminum oxide, and Carbon Nanotube to form a Nano bio composite. And why we are doing that, we will come back to the need of it, and then it has been molecular moderation has been performed for the Hydroxyapatite with Carbon Nanotube interface, because it is Carbon Nanotube which is imparting much toughness to this particular composite. You want to see, what is happening at the interface between Hydroxyapatite and Carbon Nanotube; and followed by cyto-compatibility of the overall composite, overall biocomposite whether, we are able to retain the biocompatible nature of the Hydroxyapatite. Even after reinforcing with aluminum oxide and Carbon Nanotube.

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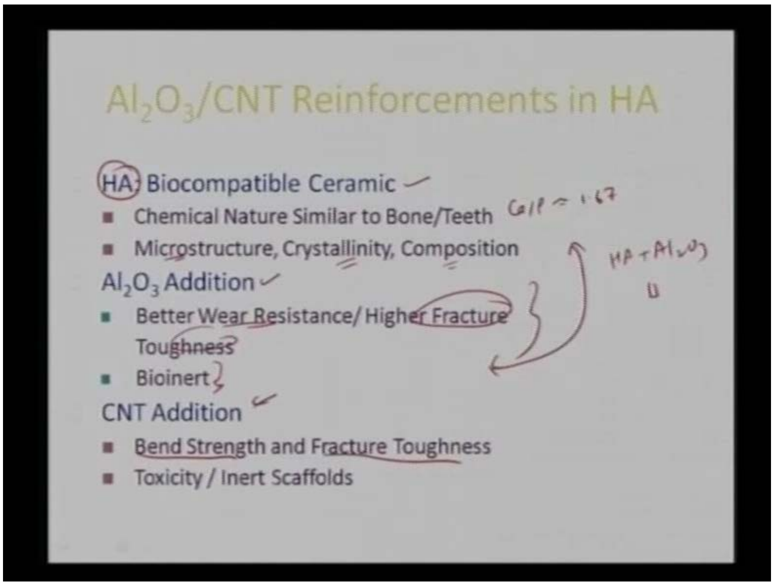

Al_2O_3/CNT Reinforcements in HA

HA: Biocompatible Ceramic

- Chemical Nature Similar to Bone/Teeth
- Microstructure, Crystallinity, Composition

Al_2O_3 Addition

- Better Wear Resistance/ Higher Fracture Toughness
- Bioinert

CNT Addition

- Bend Strength and Fracture Toughness
- Toxicity / Inert Scaffolds

$Ca/P \approx 1.67$

$HA + Al_2O_3$

The biocompatibility of Hydroxyapatite cannot be under state it, it is highly biocompatible material - it is a chemical nature similar to bone and teeth, because it is calcium or phosphate approximately 1.67 which is found naturally in apatite, and again depending on what it microstructure is - what is crystallinity, and what is composition? It can highly affect the properties of a composite.

So we need to basically control, and retain the initial ingredients of Hydroxyapatite; in terms of facility, in terms of its microstructure, in terms of its composition, and without altering them we should be able to tap it, in the final implant material what we synthesis. But the problem basic problem is Hydroxyapatite it is, is it highly bitterly in nature. Its fracture toughness is less than one megapascal route meter; it is highly highly brittle. So, we need to somehow enhance its fracture toughness properties; so for that, we have couple of choices. So, in first case what we are doing we are adding Alumina oxide. And since, also one one one more advantage to adding Alumina oxide, it is a better wear resistance. And apart from its higher fracture toughness, it it also have better tribological properties and comparison to that of Hydroxyapatite.

So, one hand we are improving its fracture toughness, because Alumina oxide is better fracture toughness to the order of 3.2 megapascal route meter, at the same time it is highly variance, because it is it is it also has very high hardness. So combination of high hardness, and high fracture toughness it can impart superior properties to

Hydroxyapatite. But the problem with this Alumina oxide is that it is bio inert in nature. It would not assist the precipitation of apatite on its surface; so that is the reason, we want to add this particular material, though we know it is bio inert. At the same time, we want to make sure bio alertness of Alumina oxide, should not interfere with the bioactivity of Hydroxyapatite.

So in this particular case, we are hiding Alumina oxide as asecondary addition to enhance its (( )) resistance, at the same time improve it fracture toughness. Despite it being the bio inert in nature. So we would just want to make a nice complementary composite, that I add certain percentage of Hydroxyapatite plus certain amount of Alumina oxide; so, I get better properties, better mechanical properties, but without detonating it Cyto-compatibility. Further, they have been some some studies which have also induced some Carbon Nanotube addition, some Carbon Nanotube reinforcement to improve its fracture toughness.

And it also been proved, that Carbon Nanotube assist self perspiration or apatite perspiration on its surface; at the same time it is improving – it is bend bend strength improving fracture toughness, but toxicity always the concerned. Because Carbon Nanotube have diameter to the order of 40 to 70 nanometer less then 100 nanometers; so it can always induce some toxicity, it can get it can even cause information, they can get accumulated certain locations liver, brain, brain any anywhere else.

So that always a problem, that anything nano once it is in body it might create some problem. But there also has been second school of thoughts, which says Carbon Nanotube is a form of Carbon. And Carbon is a basic form of life, why it should be a problem at all; they have been certain concerns, but once we are able to trap those Carbon Nanotubes, in a certain (( )) of Hydroxyapatite. We can somehow tap its bioactivity, at the same time not letting it become toxic or get loose into the body strain; and there by there by lead to the lead to it (( )) certain body or or or at at certain organ locations.

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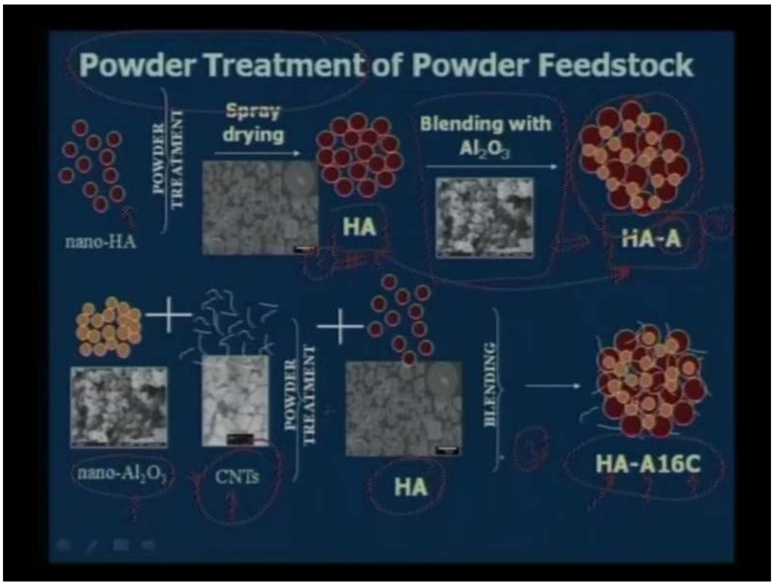

Powder Treatment of Powder Feedstock

So in this particular case, just to check how we can induce Alumina oxide and Carbon Nanotube, couple of couple of methodologies or powder treatments have been done. So coming to the first powder treatment - nano (( )) Hydroxyapatite has been taken; it has now been agglomerated to form Hydroxyapatite or nano or agglomerated Hydroxyapatite to get better flow properties.

In second case, they have been blended with micron size Alumina oxide; so we are getting agglomerate of Hydroxyapatite, which has now some micron size Alumina oxide, because if you want to dispose somehow Alumina oxide, if you want to dispose Alumina oxide in to Hydroxyapatite; we need to have it control - in a very control passion. And if you already have an agglomerate of Hydroxyapatite, then it basically Hydroxyapatite Alumina oxide, just will disperse on the surface of Hydroxyapatite. That also often agglomerate; so, if in case we want to blend them together, and then to the (( )) that might result, much better properties that what is it is being done in this particular case, that Alumina oxide has been now blended with the spraytite Hydroxyapatite.

And in second case, we also want to dispose Carbon Nanotube, because Carbon Nanotube are the one or the entities which can impart very high fracture toughness. So they they have been first of all disposed in an Alumina oxide matrix, so we get an agglomerate of Alumina oxide plus (( )) Carbon Nanotube. And now, those have been blended with the hydroxprate powder. So, we have basically a three cases – first, we only have hydroxide Hydroxyapatite without any addition; in second case, we have Hydroxyapatite plus reinforcement of Alumina oxide. So, we have blended the splited hydroxide powder with the Alumina oxide powder, so in this case, we do not have any CNT; so from this particular combination we can compared with the Hydroxyapatite and we can see, what is the role of Alumina oxide only to impart fracture toughness or improve its wear properties.

So, from jump from one Hydroxyapatite to Hydroxyapatite with some Alumina, we can comment what is the role of Alumina in terms of increasing its wear properties or wear tribology or improving its fracture toughness.

In a second case, we have both; we have Hydroxyapatite plus some Alumina plus Carbon Nanotube. So, we had…So in this particular case, we can see what is the role of Carbon Nanotube, in terms of improving its fracture toughness or wear resistance. So, in that particular manner, we can compare these three these three composites, at the same time once we were improving some property, some mechanical properties; we want to make sure that they still they still remain Cyto-compatible or biocompatible. Even after the reinforcement of nano or some micro Alumina and nano Carbon Nanotubes. So that is the overall strategy of being powder treatment, in terms of evaluating evaluating; what is the role of Alumina, and what is the role of Carbon Nanotube, in terms of attracting the Hydroxyapatite mechanical properties.

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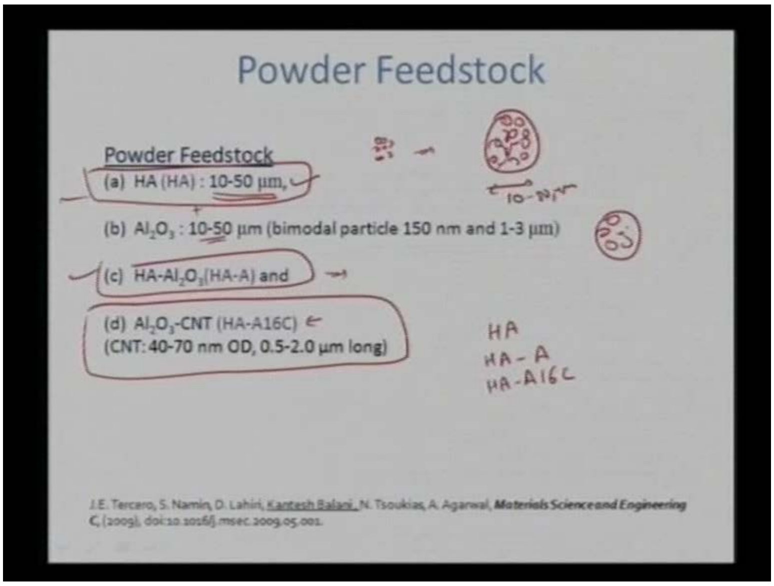

Powder Feedstock

Powder Feedstock

(a) HA (HA) : 10-50 µm,

(b) Al_2O_3 : 10-50 µm (bimodal particle 150 nm and 1-3 µm)

(c) HA-Al_2O_3(HA-A) and

(d) Al_2O_3-CNT (HA-A16C)
(CNT: 40-70 nm OD, 0.5-2.0 µm long)

HA
HA - A
HA-A16C

J.E. Tercero, S. Namin, D. Lahiri, Kantesh Balani, N. Tsoukias, A. Agarwal, *Materials Science and Engineering C*, (2009), doi:10.1016/j.msec.2009.05.001

So, we have taken powder feedstock, which is of Hydroxyapatite. Hydroxyapatite though it is, though its sizes different its in the order of couple of nanometers; it has been agglomerated as between 10 to 50 micrometers. So, initially we have fine Hydroxyapatite powders, those have been agglomerated as a powder particle which is again 50 to 45 micrometer in size; so, we we see something like this 10 to15 micrometer in size.

So it is a agglomerate, and which has some nano Hydroxyapatite available in it; in the second case we have added some Alumina oxide Alumina oxide, again it is a spray dried agglomerate. So, again you see agglomerate, but now they both have been blended in the second case. So, this is our first case, we only take Hydroxyapatite; this is the second case where we have Hydroxyapatite plus some Alumina oxide. So, in this case, we have blend them together, to see what is the effect of Alumina oxide out there; and again we have formulated it in to the order of 15 to 10 to 50 micro meter in size. And in the third case, some Carbon Nanotubes have been added; so, we see the terminology Hydroxyapatite - Hydroxyapatite plus some Alumina has been denoted by HA A; and once, we also add some Carbon Nanotube. In this case, it is 1.6 weight percent Carbon Nanotube. So, we denoted denoted as Hydroxyapatite, Alumina with 1.6 or it 16 C, 1.6 weight person Carbon Nanotube. And Carbon Nanotube as we know, they are nano entities; so, they have diameter of 40 to 70 nanometer in a length of 0.5 to 2 microns.

So, from the combination of these three, we can always assimilate are the data, and we can find out what is happening in terms of their contribution, in terms of enhancing its wear resistance or Cyto-compatibility or even changing the fracture toughness.

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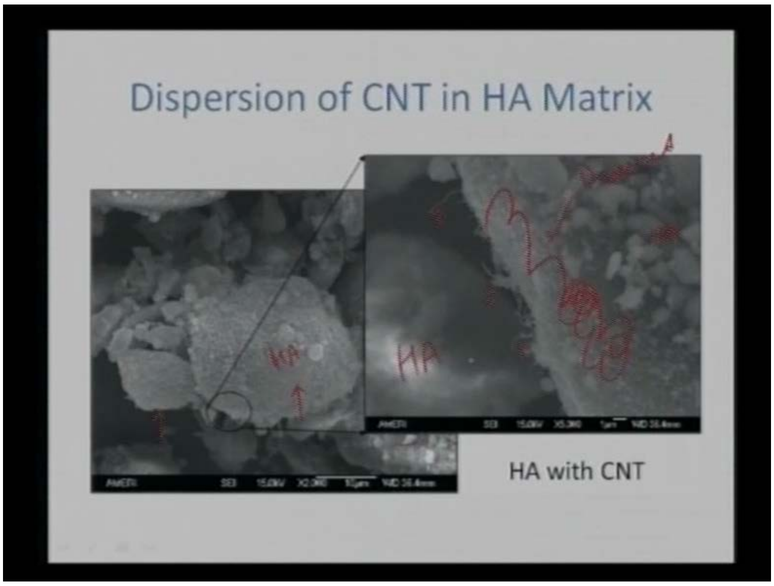

Dispersion of CNT in HA Matrix

HA with CNT

But one more part which was very very critical out here is, you have to dispose the Carbon Nanotubes. Because Carbon Nanotubes, they have such high or superior mechanical properties; they have just modeless, elastic modeless in order of 1.4 terra pascals, fracture strength of 1 to 2 giga pascals, at the same time they are very very light, the one sixth as heaviest steel.

So, if we can somehow disperse Carbon Nanotube, we can achieve very uniform properties throughout the implant material. So, somehow we want to disperse Carbon Nanotubes, but owing to their nano natures they always have tendency to agglomerate, because of their high specific surface area, they always have tendency to agglomerate, and become some sort of micron size cluster. But once we disposed the Carbon Nanotube, once we have blended them in the Hydroxyapatite matrix; it has been absorbed that this this Carbon Nanotubes, they somehow disperse automatically.

We can see the cluster of Carbon Nanotube around this region, this is already dispersed; this is again dispersed already in the Hydroxyapatite material; this is nothing but the Hydroxyapatite Hydroxyapatite crystals or powder particles. So, we have Hydroxyapatite powder particles, and we can see CNT now nicely they have dispersed either on the surface on their surfaces; and this is zoomed up picture, we show that CNT's are indeed well disperse in the Hydroxyapatite matrix. And to stress at one point the Carbon Nanotubes have not been functionalized. We have the bonds of the CNT surface, they have not been broken, and they have been not functionalized to somehow in track with the Hydroxyapatite surface. So, there is beauty of it that Carbon Nanotube without any fictionalization, it is getting dispersed in to the matrix.

So that is the one of the one of the beauty, of the CNT depression in the Hydroxyapatite matrix. This directly tells us that, there is some affinity of the Hydroxyapatite with the CNT; so in in that particular case, we might achieve enhance fracture toughness, because of CNT adhesion.

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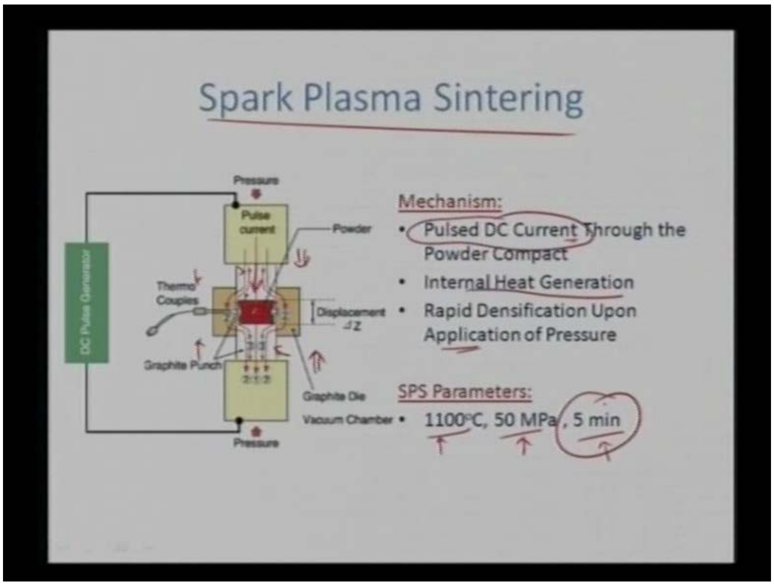
Spark Plasma Sintering

Mechanism:

- Pulsed DC Current Through the Powder Compact
- Internal Heat Generation
- Rapid Densification Upon Application of Pressure

SPS Parameters:

- 1100°C, 50 MPa, 5 min

Now this compacts or the three compacts, they have been spark plasma sintered - spark plasma sintering is a mechanism where we pass a pulsed DC current, through the powder compact. So in this case, we can see we have a graphite die, we have graphite die this is nothing but the graphite punch or the graphite die, and in this case we keep the powder this is nothing but one, so in this region we keep the powder. Once we have the powder, it is now compacted, so we compact the powder and pass up pulse DC, and because of joule heating; automatic there is some internal heat generation, because of joule heating means when we applying certain pulsed DC current, and the joule heating, we get heat generation and we compact the powder via punch, and then that results densification, once you apply the pressure.

So the temperature can be as high as in this particular case, we utilize temperatures of the order of 1100 degrees centigrade, pressures of up to 50 megapascals for duration of 5 minutes. So the comparison can occur very very rapidly, we are reaching the temperature of 1100 1100 degree centigrade, we can have heating rates as high as 100 to 200 centigrade per minute; pressure to the order of 50 megapascal, and as we see the sintering is completely within a time frame of approximately 5 minutes.

So that is the beauty of spark plasma sintering. We create a localized heating along the powder particles surface, and after that it is followed by necking and rapid sintering, because of joule heating; simultaneously, we are applying pressure to it. So we can achieve density very easily which are greater than 95 percent.

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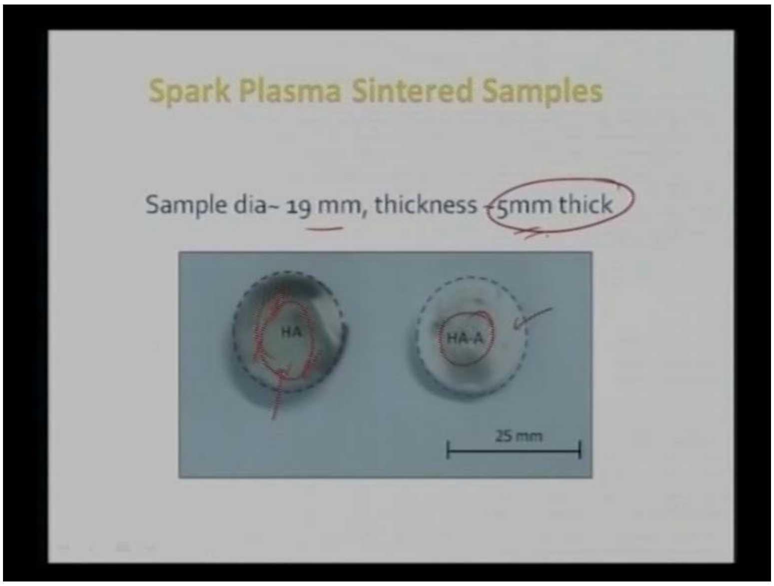

Spark Plasma Sintered Samples

Sample dia~ 19 mm, thickness ~5mm thick

And these are the spark spark plasma sintered samples: We can see the sample diameters approximately 19 millemeter, and it has thickness of approximately 5 millimeters. So, we can see the Hydroxyapatite is much more (( )), and with the addition of Alumina it is become much more wider. And this blackish color is coming, because of the graphing sheet which is kept on the top of the Hydroxyapatite powder; so they they do not very strict to the die that is the part we can see here, with sample diameters of 19 millimeters, and we can go as such as 5 millimeters in the two cases.

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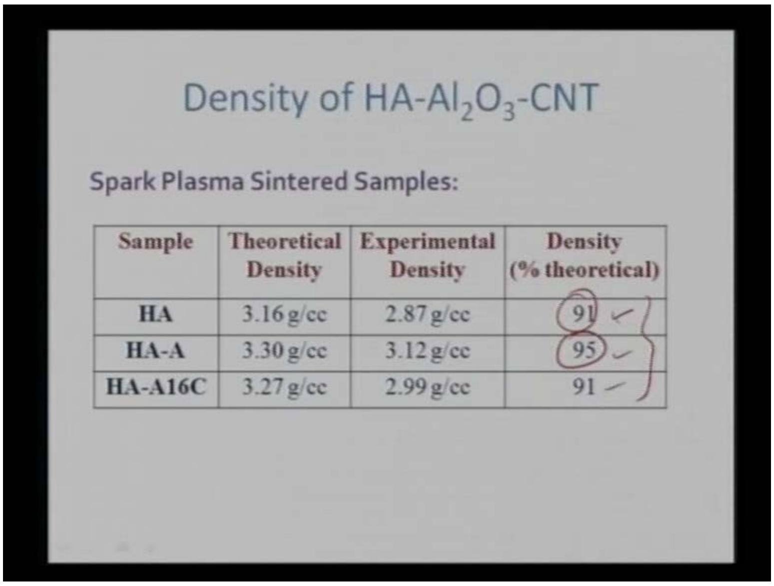

Density of HA-Al_2O_3-CNT

Spark Plasma Sintered Samples:

Sample	Theoretical Density	Experimental Density	Density (% theoretical)
HA	3.16 g/cc	2.87 g/cc	91 ✓
HA-A	3.30 g/cc	3.12 g/cc	95 ✓
HA-A16C	3.27 g/cc	2.99 g/cc	91 ✓

And as we see that densities are pretty high greater than 90 percent, and at the same time we I like we can also say that, we also want to say that that postured is one of the very critical components of estimating biocompatibility. Because if I if the cells to grow, and somehow mechanically interlock, they should be enough porosity available for the cells to interact themselves with the material.

And they can extend their fibrous arms, into porous available; so they can they can also keep getting nutrients from outside. So that is a reason, we can also say that we also need some porosity with available in the material to take care of the life of the cell. So, in all the cases we have achieved the porosity porosity levels approximately 5 to 10 percent, we can even control it using spark plasma entering. In this particular case, we have density to the order of density to the order of greater than 90 percent, and those are listed out here.

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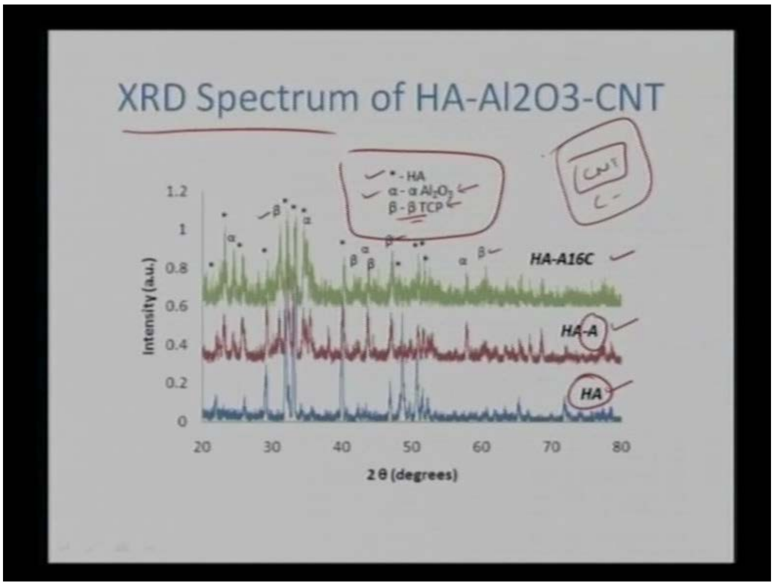

XRD Spectrum of HA-Al2O3-CNT

And once this pallet has been (( )) particular pallet has been synthesize; its (( )) spectrum was taken in this case, we can see what is happening with the Hydroxyapatite Hydroxyapatite with the Alumina and with Carbon Nanotube.

So first of all we are do we do say separate fix of Hydroxyapatite, and those of Alumina; so those part we can see very clearly. In some cases, we are also forming some minor faces of beta track calcium phosphate which is also been present here, but on one hand on the other hand, we do not see any complex phase formation; it has a very high crystallinity as we see from stronger or shorter peaks; if the facility is very very high, secondly we are not forming any complex phases between Alumina, calcium Aluminates or something like that we are not forming at all.

Also we are we are retaining the crystals structure of Alumina. It was alpha and it is remained alpha even after sintering, there is no other formation of any gamma any other meta stable phase; so from XRD we can say that there is no formation of any complex phase, and how the initial phases they have been retained. Though there is some formation of beta tricalcium phosphate. So this tells that this happening, because of the rapid processing time which is available for the spark plasma sintering. Because our entire process is get completed in 5 minutes. We are heating the particular pallet, apply certain pressure and then we complete the process by holding it, the dual time of approximately 5 minutes of 50 megapascals; so we are able to complete the process in very short duration.

That is the reason, this is not enough time available for the phase transformation from say alpha Alumina to gamma Alumina or formation of or chances of inducing any chemical reaction between calcium Hydroxyapatite and Alumina oxide; so there is no formation of calcium eliminates or any such complex entities.

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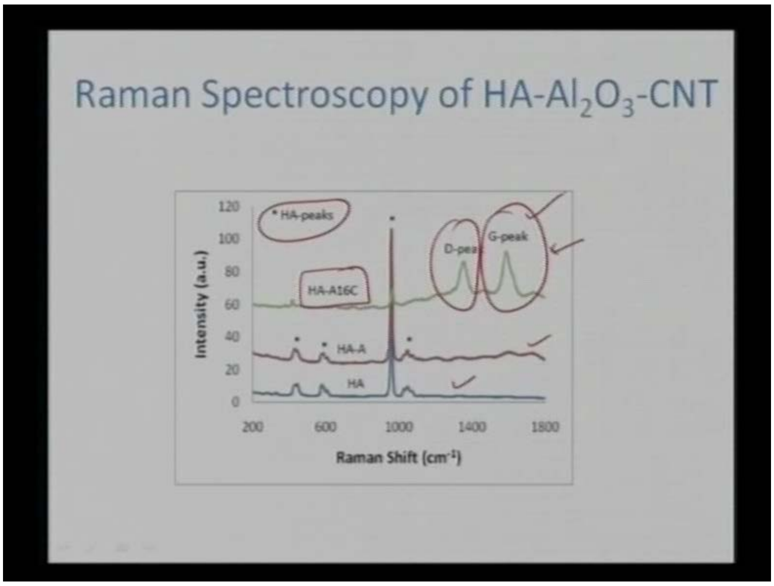

Raman Spectroscopy of HA-Al_2O_3-CNT

But one thing is note here is, in the XRD spectrum is we do not see any CNT peaks or do not we do not see any (( )) as well. So, it means that we have to somehow say to verify that wherever to retain the Carbon Nanotube, in order to in order to in order to tap the advantages which can which we can get from the CNT reinforcement. So, in this case we are not able to see any graphite or Carbon Nano peaks; so that is the reason we have done raman raman spectroscopy, and from that we can clearly see that the graphitic peak is now retain in the HA-A16C pallet. So, this is for Hydroxyapatite we do see some Hydroxyapatite peaks, this is again for Hydroxyapatite with some Alumina; so we are seeing many Hydroxyapatite peaks, because Alumina oxide peak is very very fable. And once we add Carbon Nanotube, we can see similar D and G peaks; so the G peak is basically retain, that tells the graphtic of Carbon Nanotube are intact even after spark plasma sintering. So spark plasma sintering is not inducing any damage to the Carbon

Nanotube, and we are able to retain the Carbon Nanotube even after spark plasma sintering.

So, once we are able to retain the Carbon Nanotubes, then we can expect to, then we can expect enhance mechanical properties or enhance pressure toughness or enhance tribological properties from arising from the Carbon Nanotube.

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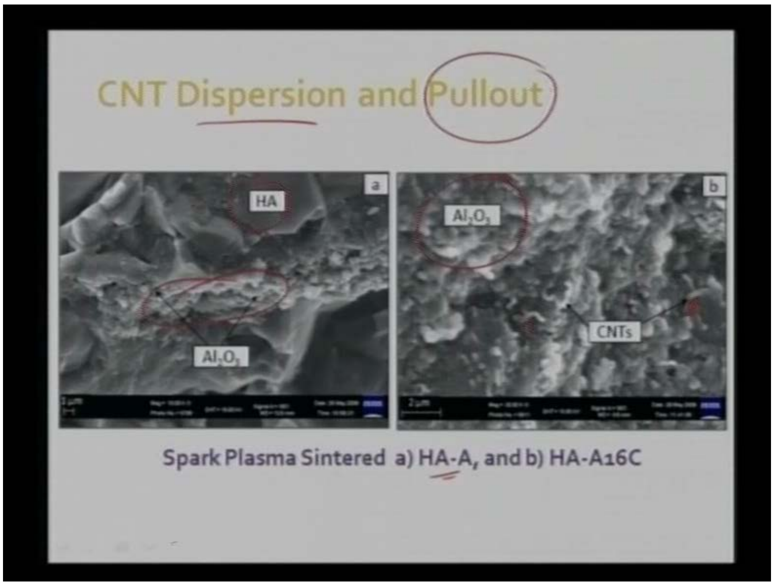

CNT Dispersion and Pullout

Spark Plasma Sintered a) HA-A, and b) HA-A16C

This is the particular microstructure which shows that we have CNT dispersion, the same time we also do see some pullout. So in first case we have Hydroxyapatite with some Alumina; so we can see that Hydroxyapatite grains are out there, and we have Nano Alumina oxide which was now dispersed in the Hydroxyapatite grains.

The second case we can also see, there is some CNT pullout or Carbon Nanotube pullout which is now in the Hydroxyapatite, and the Alumina oxide composite; so, we do CNT pullout is occurring; that means, that now some extra energy has to be supplied in order to break the Carbon Nanotube, because Carbon Nanotube has very high structure style. So, there is there definitely we have to supply some extra energy, in order to fracture Carbon Nanotubes or induced their pullout. So this pullout is telling two things - First of all CNT very dispersed in the matrix, secondly it will it will also enhance its fracture toughness. That those are two things we can inform from this particular (( )) image. So, we are seeing that CNT s, it is showing pullouts and it is very well dispersed throughout the matrix.

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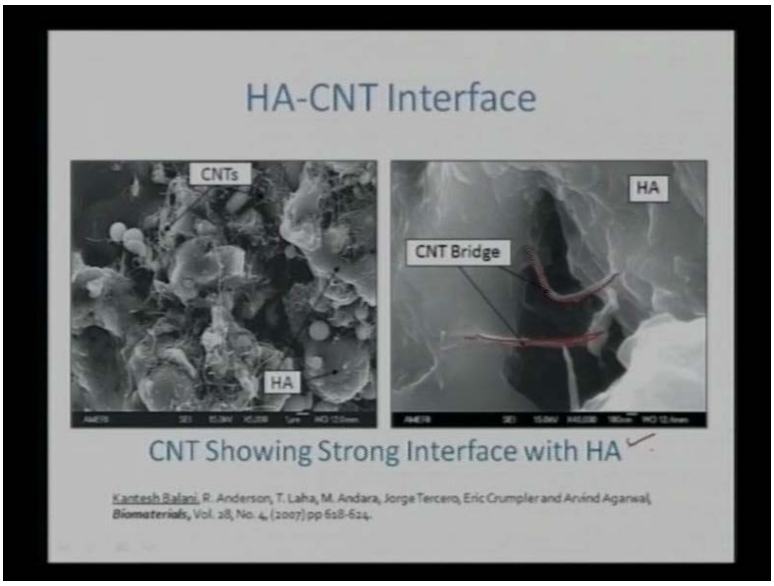

HA-CNT Interface

CNT Showing Strong Interface with HA

Kantesh Balani, R. Anderson, T. Laha, M. Andara, Jorge Tercero, Eric Crumpler and Arvind Agarwal, **Biomaterials**, Vol. 28, No. 4, (2007) pp 618-624.

And it has also been shown in by some researchers that CNT is they also attend to spread out, and they enhance fracture toughness by creating some CNT s bridges, as we see here. So, this CNT bridging is also very very essential, because it would not let the two power of particles, separate out so easily. And again the fracture will also induced some energy absorption for enhancement of the fracture toughness; so that is what CNT does by either diverting the crack itself, if crack is generating it will divert the crack, it will restrain two powder articles or two splats and then it will provide its own energy, in terms of in terms of basically preventing them - preventing the separation or enhancing the fracture toughness.

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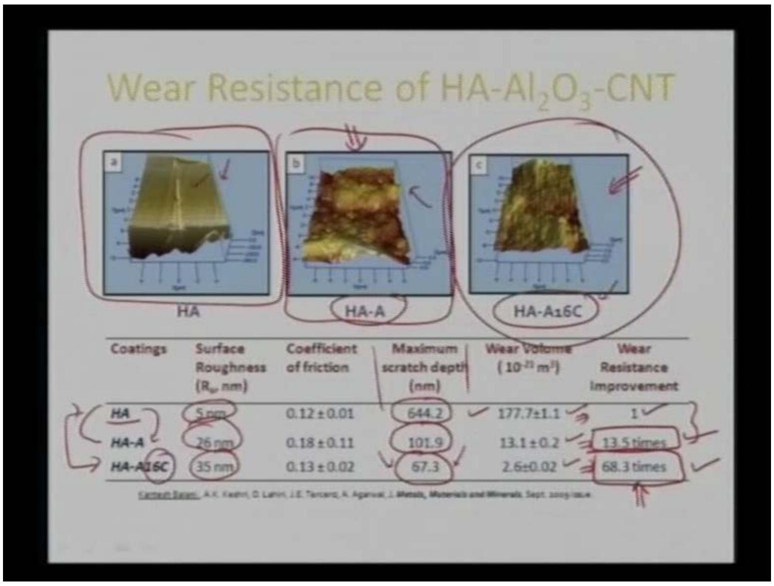

Wear Resistance of HA-Al_2O_3-CNT

Coatings	Surface Roughness (R_a, nm)	Coefficient of friction	Maximum scratch depth (nm)	Wear Volume (10^{-21} m^3)	Wear Resistance Improvement
HA	5 nm	0.12 ± 0.01	644.2	177.7±1.1	1
HA-A	26 nm	0.18 ± 0.11	101.9	13.1 ± 0.2	13.5 times
HA-A16C	35 nm	0.13 ± 0.02	67.3	2.6±0.02	68.3 times

Additionally it has been also absorbed, that they can also improve the fracture, the wear resistance of the composite. So this is a particular profile which has which has been Nanoscratch, so we see that we have certain profile. So, Nanoscratch has been done on a surface of Hydroxyapatite out there, and from this we can see a certain depth which results, so this is the depth of Hydroxyapatite only, and once we start adding some Alumina oxide on to it. We see that there much more roughness - the roughness part has being increased drastically, in the HA-A or the Hydroxyapatite which is now been reinforcement with Alumina oxide, so the roughness part is highly increased, because we are adding; some micron size, Alumina oxide on a add on a in a Hydroxyapatite matrix; additionally, we also have some induction of some Carbon Nanotubes, we can see the roughness part is also increasing initially with 5 nanometers roughness. We can go for very fine polishing, and as we add Alumina oxide - the surface roughness has now increased; the average roughness and once we had much more Carbon Nanotube, one more reinforcement of Carbon Nanotube the roughness is increased further.

But more than that, once we are doing a Nanoscratch, we can see very nicely that the maximum scratch type which was so obvious in Hydroxyapatite, it has now reduced very drastically; approximately six times.

Further once I have, once we are adding much more Carbon Nanotube to it, along along with Alumina oxide thus maximum (( )) decreased further. It means, now where should I have gone to a very low level. Eventually, depending on the crack lamp, and the crack depth where volume has been calculated; once the where volume has been calculated from that, we see how much is the reduction in the wear volume. And that gives us the wear resistance improvement.

So we can see with Alumina oxide at addition, we are seeing improvement of approximately 13.5 times. And further addition of only 1.68 percent of Carbon Nanotube, we are getting improvement of approximately 68.3 times. That part we can very, very nicely say, once we are riding some Alumina oxide. Alumina oxide is a ceramic which is a very high hardness, and very high fracture toughness. So, it somehow restrains the damage which is imparted onto onto it, and its support Hydroxyapatite matrix. Hydroxyapatite matrix alone it is not that, it is though it is ceramic, it does not have enough fracture toughness, and hardness to support its integrity in terms of wear; so it basically wears out very quickly, and it shows a very high wear volume.

But once we adds some Alumina oxide to it, it is against the ceramic with higher hardness and higher fracture toughness, its somehow supports or resists for that wear of the matrix. And that is how, it is shown in enhancement of approximately 13.5 times, further with addition of Carbon Nanotube to it. If we start Carbon Nanotube to it, what happens Carbon Nanotube acts also as a lubricant; graphing graphing graphing layers have been used in the lubricants to some of, because of its higher higher modulus; it is a higher fracture strength, also (( )) acts as a lubricant. So, because of all combination of all the three, we also have an addition of aluminum oxide into it, somehow it has increasing the wear resistance by more than 68 times.

So we can see that change from HA HA-A, Hydroxyapatite to that that of addition of Alumina, we are getting improvement approximately 13.5 times, but once we start adding Carbon Nanotube to it, only 1.6 weight percent Carbon Nanotube from 13.5 we are getting improvement of approximately 68.3 times.

So approximately five times more improvement, we are getting just by adding a little Carbon Nanotube into them. That is the beauty of this particular composite, that we can get exceptional or very high very better tribological properties; once we add Carbon Nanotube and macron size Alumina in the Hydroxyapatite matrix.

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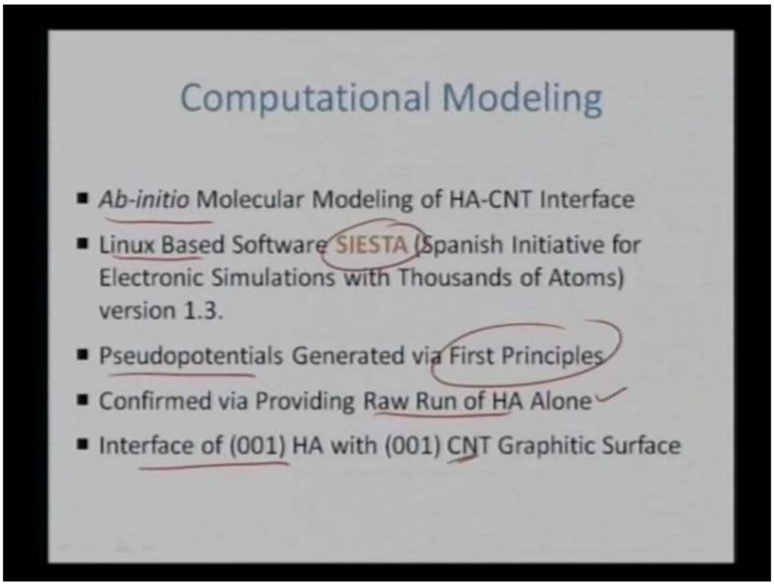

Computational Modeling

- *Ab-initio* Molecular Modeling of HA-CNT Interface
- Linux Based Software SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) version 1.3.
- Pseudopotentials Generated via First Principles
- Confirmed via Providing Raw Run of HA Alone
- Interface of (001) HA with (001) CNT Graphitic Surface

So to see what is CNT doing on on to the Hydroxyapatite; some computational modeling has been done. So in this particular case Ab-initio molecular modeling has been utilized. Ab-initio means, we are utilizing only the electronic state of a particular material like, Hydroxyapatite is a complex CA 10 PO 4 whole 6 OH whole twice. So in this case, we define the properties of a particular material or a particular component just by the electronic configuration. Like, calcium we will be define by its electronic configuration 1 is to 2 is to the way it goes, hydrogen by one is to one; hence so on. So, only input we require is the electronic configuration, and based on that Linux based software has been used which is SIESTA, which is called Spanish initiative for electronic simulations with thousands of atoms.

So in this case, we can use utilize many more number of items, and see their interaction what is how the interaction is happening using a Linux based software, and then the pseudo potentials are generated. In this particular case, we assume the many electron problem as a single electron problem. Then this case, we are avoiding so much interaction of so much electrons, and we replacing that by interaction with only representing a particular or a complex material, complex item with so many electrons by a single electron. So, we assume that say for oxygen we have eight electrons, so we assume that all the eight electrons, they are now being replaced by one electron which is behaving similarly, as an average all eight electrons well.

So that is the reason, we create some pseudo potentials via using those first principles, and then we confirm those positions via running by doing a raw run of Hydroxyapatite alone. So we confirm that the final coordinates of all the calcium oxygen, phosphates, hydrogens what we get in the structure, they match with the theoretical values of the Hydroxyapatite crystal. So by that, we have confirm the pseudopotential that they are correct or not; and then we have created an interface of Hydroxyapatite with Carbon Nanotube to see what else happening at the interface. Why CNT is getting so disperse so nicely, and why there inducing enhance fracture toughness, because of CNT addition. So an interface has been created which will result, which will tell us what is the interaction happening between the two.

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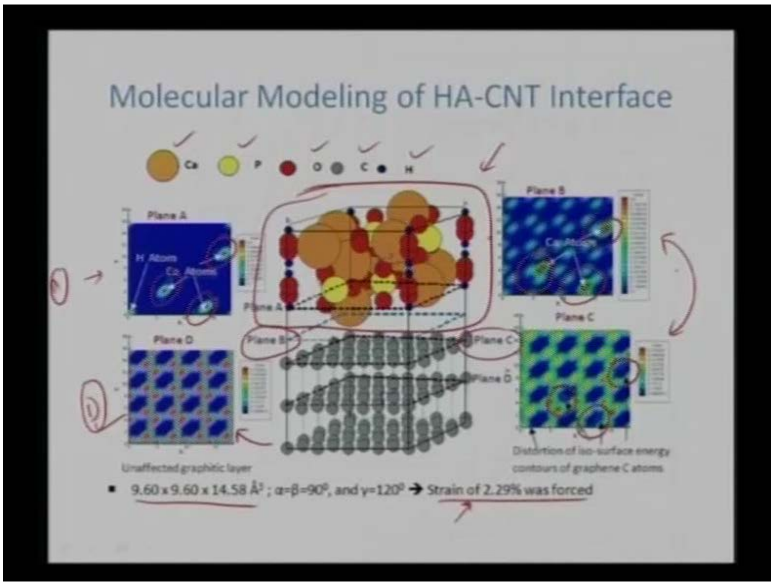

Molecular Modeling of HA-CNT Interface

- 9.60 x 9.60 x 14.58 Å³ ; α=β=90º, and γ=120º → Strain of 2.29% was forced

So this is how the crystal appears finally, this is one what we have the Hydroxyapatite crystal, and this is the graphitic planes what we might expect in the Carbon Nanotube. So in this case, we have all the items calcium, phosphorous, oxygen, and Carbon and hydrogen. So that those those all are appearing in the Hydroxyapatite and the Carbon Nanotube interface, and since the interface between those two it is not exactly matching.

So strain of 2.29 percent has been enforced, and a crystal of approximately approximate size 9.6 by 9.6 by 14.58 armstrong cube has been created. And what we see here is, that calcium the Hydroxyapatite has calcium atom on its surface - those are here, and if you create certain place, like this is the the terminating plane of Hydroxyapatite. So it has some surface calcium atoms, and these are the unperturbed graphitic layers.

So we do so here, very regular symmetry or the regular geometry of a of the Carbon atoms, on the on a particular plane, those are unaffected, (( )) we start going near the interface. Like plane C or plane B which is exactly at the center, we see that plane B and plane C they start showing some effect or some destruction of the iso surface energy concludes. It means, there is some overlap of the electron density between hydro calcium atoms, and those of Carbon atoms. So, those interactions we can see out here, out here and we can see that there is some perturbation which is happening by destructing the iso-surface energy contribute, it means there is some overlap or some interaction happening between the electron cloud of calcium and that of a Carbon .

It means there is some sort of a bonding which is happening between the two, and that is resulting the automatic dispersion of Carbon Nanotube on the Hydroxyapatite surface. So that is the beauty what we are seeing in this particular case, that we are able to see dispersion - very nice dispersion of this Carbon Nanotube on the Hydroxyapatite surface. So, overall we could see that we have done Ab-initio Ab-initio molecular modeling.

So, we input all the all the data is basically coming from the electronic configuration of calcium of phosphorous of oxygen of Carbon and hydrogen, and then an interface has been created between them. And since the interface cannot match exactly 0 0 1of Hydroxyapatite and 0 0 1 of CNT cannot match.

So, a strain has to had to introduced, and this strain will allow the overall crystal to match perfectly; and from that there are certain planes which are unaffected planes those are a n plane a n plane d, so those are un remain unaffected they are much far apart from the interface; whereas, soon as we start coming near the interface, we see some overlapping of the electron cloud or the iso surface energy is now getting perturb, because of the interference from the calcium surface calcium atoms. And that is the reason, that it shows some affinity towards the Carbon Nanotube, and then we see a nice distribution of Carbon Nanotube with Hydroxyapatite.

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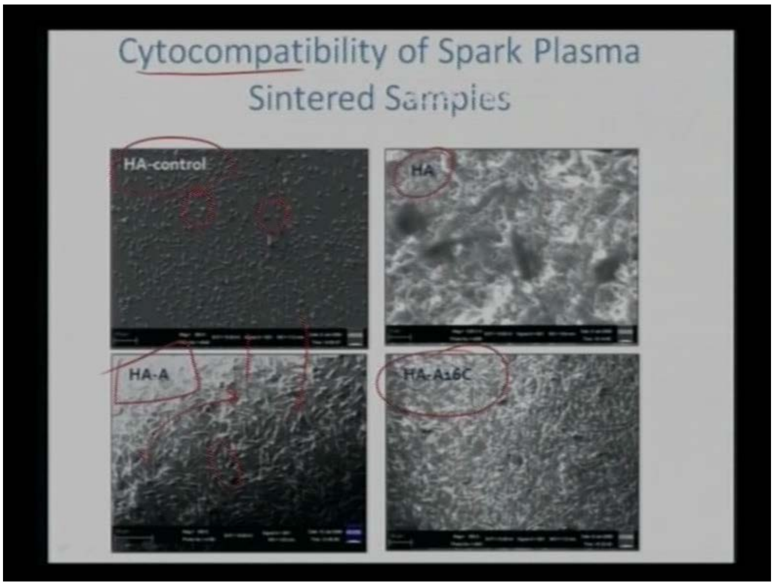

Cytocompatibility of Spark Plasma Sintered Samples

And once and once, we have confirmed the nice interaction which is happening between the CNT’s and that of a Hydroxyapatite, we also want make sure what is happening in terms of their bio Cyto-compatibility.

So a very nice sample has been obtained; that we taken a Hydroxyapatite control sample - it is a negative control, so we can see that l nine to nine cells or the nice fibroblast have been growing very nicely on the surface of Hydroxyapatite, which is a control sample and the same thing we are seeing in the Hydroxyapatite, as we as we add Alumina Alumnia in to it. We can see the density has gone gone approximately similar. And also with the addition of Carbon Nanotube, we are seeing approximately similar density or higher density; so this tells directly that, we are affecting or we are not inducing any toxicity by adding Alumina oxide or by adding Carbon Nanotube into the matrix.

So this case we can see very nicely, in the Hydroxyapatite we have nice flow of nice spread of all the cells fibroblast, and there couple of things which we can note here is, first of all we do see some formation of self, and also some which are spread out and there are some cells which are still globular in nature. So in this case, we can see some cell which are much more globular in nature, and some cells which are still spreading out.

So generation of this kind of morphology is very very common, that we do see some cells which remain globular and some basically spread out. The spreading of cells is limited to, once they find some friendly surface friendlier surface they tend to increase their surface area, because that has them to interact with the surface nicely, because once we have higher surface area and then they can interact to a larger extent with the underlying material, (( )) tend to spread and even do not find the surface to be friendly, they remove remain globular. Because now they they have the interacting surface area is very very low. Because for its fair and for a plane, the overall contact area will be just like a point. So, in those cases once they remain globular, they do not find the surface to be friendly enough or when the surface is not that by a Cyto-compatible; it tends to remain globular, but in the other cases we have seen similar (( )) similar some globular globular cells as well, but most of the cells are spreading out in their enhancing enhancing in the lengths.

So, it means that the cells are not only adhering, they are also growing. So, we can see three things. The surfaces Cyto-compatible Cyto-compatible cells of finding the surface Cyto-compatible, and because of that they are spreading. And once they are spreading out, they also tend they are also tending to grow further. So unhanded growth has been also observed in this particular cases.

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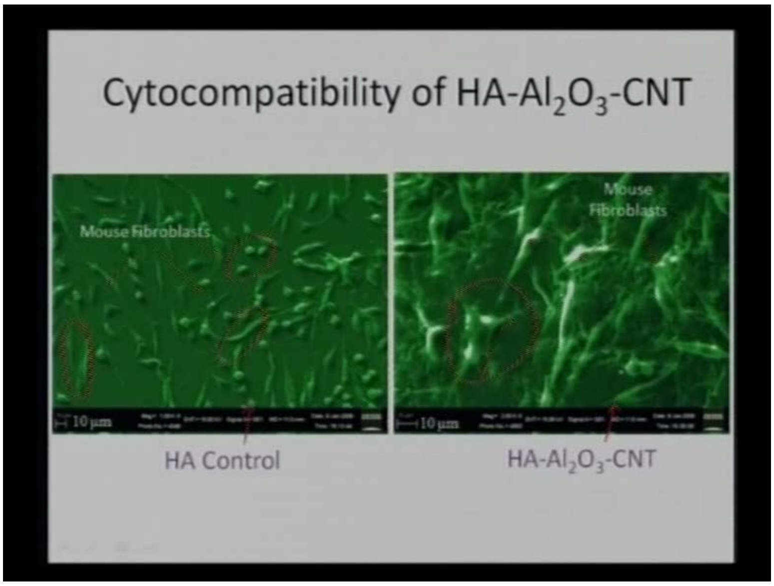

Cytocompatibility of HA-Al_2O_3-CNT

So, we do see some for a little higher verification, we do see some globular cells which are out there; and we also see some spread out cells. So we can see most of the cells they are now spread out. So in this case, this is the control sample and this is one with the

CNT; so we can see that cells are basically spreading out like this, they are extending their arms and their their their overall surface has been now enhance, because of this and that what we are able to see in this particular case.

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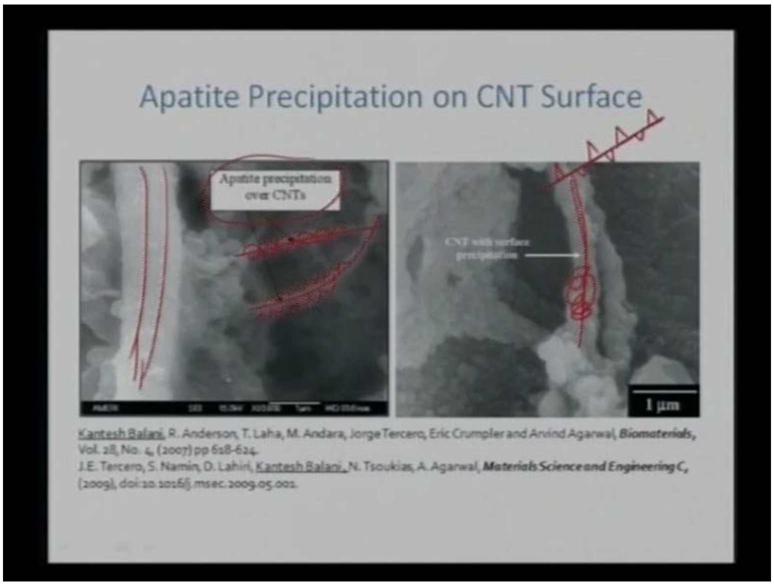

Apatite Precipitation on CNT Surface

Kantesh Balani, R. Anderson, T. Laha, M. Andara, Jorge Tercero, Eric Crumpler and Arvind Agarwal, ***Biomaterials***, Vol. 28, No. 4, (2007) pp 618-624.
J.E. Tercero, S. Namin, D. Lahiri, Kantesh Balani, N. Tsoukias, A. Agarwal, ***Materials Science and Engineering C***, (2009), doi:10.1016/j.msec.2009.05.001.

So, that tells us cytocompatibility has been retained, even after the reinforcement reinforcement with the Carbon Nanotube. So in this, case we can see that CNT is they not only enhancing fracture toughness or there do not enhancing the mechanic tribological properties, but they also assist in the apatite precipitation on its surface. So, in this case we can see, we have the cells which are basically like this. And then we also have some Carbon Nanotube, and over that we have seen some precipitation of apatite on its surface. And that part has also been confirmed by a couple of researchers, such as laura, and haden, hadens group. They do see some bard wide kind of a structure, that they have CNT, and over that they see very nice precipitated apatite kneaders on the surface of Carbon Nanotubes.

And the same structure is also observed in this particular case, that we have Carbon Nanotubes they they have very nice dispersion of or precipitation of apatite on its surface. So, one thing is very clear, because of higher surface area of available for the Carbon Nanotube, it is somehow assisting the precipitation of apatite; and why the precipitate apatite precipitation is very very important, because now that is what required for the bone growth.

So, once we have available CNT surface with a particular implant implant material, it will also assist the a precipitation of apatite or the or the generation of new bone. So, there are many advantage which are associated with Carbon Nanotube that apart from improving improving that tribological properties dramatically, it is also assisting the apatite precipitation. So, it confirms that once CNT is they are entrapped in to a particular matrix, such as Hydroxyapatite they are not being toxic any more.

So in this particular case, we can say very strongly that we have CNT's, and they are somehow encouraging the precipitation of apatite on its surface. So, in this particular case, we also see some CNT's they are totally covered with apatite. Had they being toxic they would allow the precipitation of apatite, they will just kill the cells which are already there.

So in this particular case we have osteoblast, and then osteoblast those osteoblast they are growing very nicely, because we also see some precipitation of apatite crystals on the Carbon Nanotube surface. So, that part is very very clear, and we do we do not see any the dead cells on nearby its vicinity.

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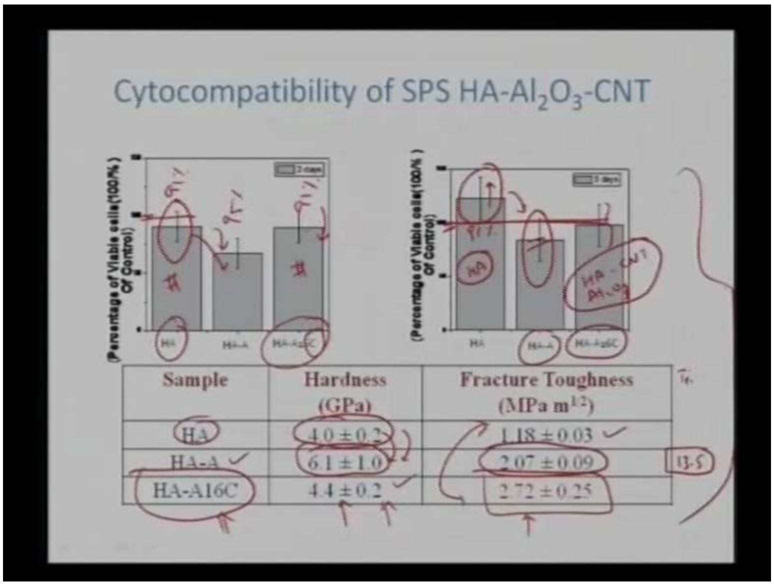

Cytocompatibility of SPS HA-Al_2O_3-CNT

Sample	Hardness (GPa)	Fracture Toughness (MPa m$^{1/2}$)
HA	4.0 ± 0.2	1.18 ± 0.03
HA-A	6.1 ± 1.0	2.07 ± 0.09
HA-A16C	4.4 ± 0.2	2.72 ± 0.25

Further there has been MTT as says or quantification of them of the viable cells has been done. So in one case, we see Hydroxyapatite which is approximately control sample is taken as 100, and then we have some Hydroxyapatite, because of their porosity we can also see that Hydroxyapatited approximately, similar to that of the control sample;

whereas, for Hydroxyapatite with Alumina it is showing lower percentage of viable cell that might be happening, because Alumina oxide is bio-inert in nature. So that part we can say, that because of the inertness of the Alumina oxide. It is somehow reducing the viability or the cell viability which is available.

At the same time the particular structure was highly dense. It is density was 95 when comparison to other 2 for Hydroxyapatite the density was around 91 percent for for the with Aluminates was approximately 95 percent, then again with CNT is 91 percent. Somehow porosity is also playing a role, that the cells are not getting compatible enough in the highly dense region, that is Hydroxyapatite with Alumina in it. And this results are for the three days; and we do see that the similar nature is also being renewed by the Hydroxyapatite with some Alumina and Carbon Nanotube.

So in this case also, because of higher porosity; we can say that the cells are finding themselves comfortable; ahead there been some toxicity associate with Carbon Nanotube, we should see a decrease in the cell viability. But now, this is now much more in compared it to do what we are observing for the Hydroxyapatite alone alone. Later on definitely we can see the the Hydroxyapatite alone, the cell viability has gone drastically up; the control sample is generally dense and with enhance porosity, because its 91 percent dense we do see much enhancement in the cell viability. It means, porosity also is one of the very critical features or parameters, in terms of dictating the cell growth. Further with addition of Alumina oxide it is again very very dense - Alumina is bioinert in nature is always showing a reduced response, (( )) cell response in comparison to the other two pallets.

Further for Hydroxyapatite with some (( )) addition, this now catches up with the standard approximately 98, 99 percent; and then somehow it is catching up with what was available for the dense Hydroxyapatite. So, this tells very clearly that the sample with some CNT inert - with some Alumina in CNT element is a no way inferior; in terms of Cyto-compatibility. At the same time, it is inducing tribological resistance of more than 65 times.

So that is the beauty of it, that we are attain a we are able to attain similar Cyto-compatibility with much enhance tribological response, tribological resistance. In once we add some Carbon Nanotube in to the matrix. And that thing all is achieving, we are able to achieve that we have Hydroxyapatite, we have hardness of over approximately 4 gigapascals; once we add some Alumina, we see much enhancement in the hardness. And much enhancement in the fracture toughness as well.

But it now, compares lesser in terms of Cyto-compatibility. But it is definitely superior; in terms of the mechanical properties, as well as the tribological properties. So in this case, we are achieving improvement in the fracture toughness or the tribological properties or the wear we are observing enhance wear resistance, and the wear volume was decreased by 13.5 times with addition of element. That is the advantage with Hydroxyapatite, we are certain properties hardness is 4.0 gigapascal, fracture toughness 1.18 megapascals root meter.

And once we add Alumina oxide to it, properties are somehow dramatically enhanced, the hardness increases to 6.1, approximately 50 percent improvement, and we also see improvement in the fracture toughness, approximately again less approximately 90 around 80, 90 percent improvement in the fracture toughness, we are getting automatically with the analog side addition; but as soon as we add even little amount of Carbon Nanotube 1.6 weight percent, the hardness is somehow increased by approximately 10 percent and we do not care much about the hardness, because we are able to achieve the similar cytocompatibility as that of a standard Hydroxyapatite of a dense Hydroxyapatite so that when we are able to achieve hardness similar to that what we can get for the Hydroxyapatite, but know the fracture toughness, so that is what the limiting factor for Hydroxyapatite application.

We can achieve fracture toughness improvement of more than 100 percent; we are approximately 1.3, 1.4 the approximate improvement in the fracture toughness is approximately 2.3 times or more than 100 percent improvement. So that is the criticality that we can achieve or we can attain by the Carbon Nanotube addition, addition in the Hydroxyapatite matrix; so that is the overall philosophy of using alumina as well as Carbon Nanotube in terms of improving the hardness, fracture toughness, maintaining the cytocompatibility, and improving the tribological properties by more than 65 times. So that is the overall theme of this particular spark plasma sintered samples.

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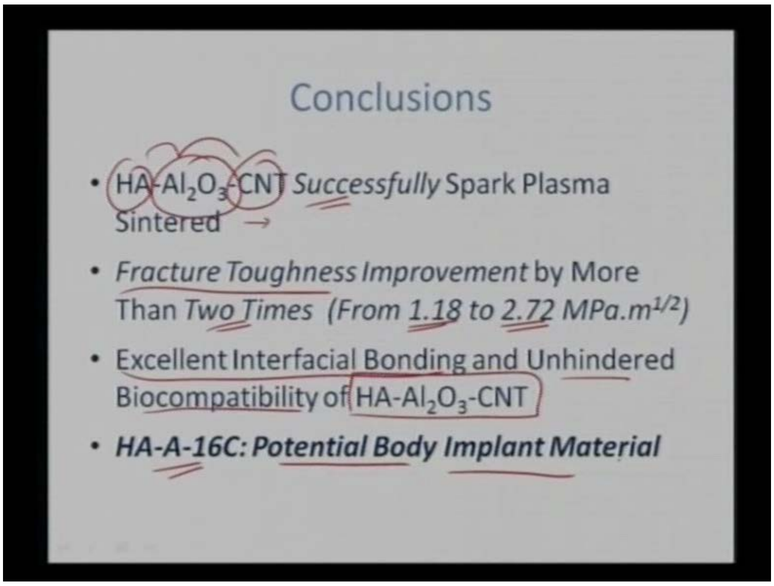

Conclusions

- $HA-Al_2O_3-CNT$ *Successfully* Spark Plasma Sintered →
- *Fracture Toughness Improvement* by More Than *Two Times (From 1.18 to 2.72 MPa.m$^{1/2}$)*
- Excellent Interfacial Bonding and Unhindered Biocompatibility of $HA-Al_2O_3-CNT$
- ***HA-A-16C: Potential Body Implant Material***

So first of all the Hydroxyapatite, because reinforce with aluminum oxide and Carbon Nanotube, it was successfully spark plasma sintered, because being able to do that also is very critical, because the sintering temperatures for all of them are very, very different; so Hydroxyapatite is different, polymer oxide is different, for CNT it is different. So once we are combining all of them, it becomes very, very difficult to maintain a particular parameter, which can sinter all of them together, and enhance very nicely uniformly dispersed manner; once we are able to disperse the CNTs, disperse the alumina oxide in Hydroxyapatite matrix, we can attain uniform properties; so that is the one of the key essential or the key or the essential parts of of spark plasma sintered that we are able to achieve the nicely dense, compact or a pallet of Hydroxyapatite with alumina oxide in CNT, and at the same time, we are also maintaining certain porosity in to it, and that is assisting the in growth of cells.

And secondly, we are also able to improve the fracture toughness by more than two times, so once we are adding Carbon Nanotube, we can increase the fracture toughness from 1.18 to approximately 2.72, it is approximately 2.3 times improvement; and that all is happening without deteriorating the cytocompatibility. So that is achievement in itself that we are able to achieve excellent interfacial bonding with unhindered biocompatibility of Hydroxyapatite, which is now reinforced with the alumina oxide and Carbon Nanotube, so this particular material can serve as a potential implant material, that is the beauty of this overall structure.

So in this particular lecture, we learnt about what is Hydroxyapatite, and it is a it has a chemical structures for chemical composition similarly, that of bone and teeth, and then why do at alumina oxide, because it has much superior hardness, and it also has much better fracture toughness, so it can eventually lead to enhance tribological properties, but the problem with that it is bioinert in nature; so that is reason, we can also add Carbon Nanotube to it; Carbon Nanotube they are bioactive in nature, and they lead to apatite precipitation on its surface; somehow they can enhance the mechanical properties without deteriorating the cytocompatible properties.

So it was followed by computation modeling as well that we want to see how the CNTs are dispersing on the Hydroxyapatite surface, because we saw the dispersion of CNT without any fictionalization on the Hydroxyapatite surface, and then this composite was was spark plasma sintered, after spark plasma sintering the properties came out to be much more superior with the alumina oxide as addition, the hardness was improved by more than 50 percent, fracture toughness almost doubled, and with further addition of Carbon Nanotube, we saw the hardness hardness was basically approximately similar 10 percent improvement, but fracture toughness improved by more than two times; and it was followed again by the tribological properties, and in the in that we see that alumina oxide can improve the wear we can reduce the wear volume by more than 13 times, because it is high, it has very high hardness, it has very high fracture toughness. So it is somehow improves the tribological properties.

But further addition of Carbon Nanotube, Carbon Nanotube can act also as a lubricant, in addition to the reinforcement, which is being provided by the aluminum oxide, so overall property was increased by more than 65 times, so this overall combination of Alumina oxide and CNT act synergistically in the Hydroxyapatite matrix to improve its fracture toughness, but without deteriorating the cytocompatibility. So with this I basically close my lecture, thank you.