

Advances in Additive Manufacturing of Materials: Current status and emerging opportunities

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Lecture 16

We will continue with this scientific case study on the binder jet 3D printing of ceramic materials. This is one of the ceramics which has also attracted significant attention in the biometrics community, (Sr, Mg)- phosphate. In the last lecture, you have seen the experimental study outcome for the binder jet 3D printing of the zirconia based materials. Now you will see more on the phosphate based materials how the binder jet 3D printing was utilized. let us recapitulate the fundamentals of the ink jetting of biomaterials or ink jet printing or binder jet 3D printing as I said multiple times in last few lectures they are all synonymous. What is important is for you to remember, this binder formulation, how binder jet is ejected, the impact the materials are powder bed and that they get infiltrated into the powder bed.

in most of the cases that what we have used is thermal drop on demand type of approach. this is the drop on demand 3D inkjet printing. In several biomedical applications calcium phosphates. which have very close similarity with the inorganic constituents of the natural bone that have been very widely investigated.

But magnesium phosphates as I said in one of the earlier lectures that magnesium as a biomaterial also has attracted lot of attention. So magnesium phosphate based materials has also attracted attention because of the absence of low soluble phases and higher biodegradability than calcium phosphate based materials. strontium ion incorporation has specific benefits or advantages, one for osteoporosis treatment and also another one for accelerated bone cement. This schematic essentially shows that one of our earlier work which is published in biomaterials that strontium containing glass ceramic materials from our group in collaboration with UK University, University of Birmingham that we have implanted into the rabbit model in that this is the femoral defects in the rabbit model. And then we have observed that animal's activity and then we have sacrificed after 12 weeks.

Then we have done both the 4 weeks and 12 weeks samples we have retrieved after sacrifice in the animal. Then we have done extensive 3D micro computer tomography analysis trying to see that how bone grows into these kind of materials. Now if you look

at that calcium phosphate but magnesium phosphate scaffolds in terms of their specific advantages in calcium phosphate you have alpha or beta tricalcium phosphate that is possible. You have also TTCP like apatite is hydroxyapatite but brucite and monetite is also possible. In magnesium phosphate you can use either pure or substituted and then you can get struvite is one of the phases that you will also notice in next few minutes time.

One of the approach that many of us believed at that time when we started this research is that why not calcium and magnesium phosphate together and then we can see that how the mixed phosphates can be 3D printed and how their structure can be printed. this was the first type of materials that we have used but also we have also further found out that how to dope the strontium salt into it and so the strontium-doped magnesium phosphate is one of the materials that we have tried. This post-processing of the 3D binder jet printed scaffolds, so I would repeat or I would like bring to your attention the fact that all the scientific case studies whatever you have seen so far and what you will see in this particular case study and further, that we not only have shown you that how different kind of binder can be formulated but also have shown you that how to tailor post-processing treatment of these scaffolds. For example, if you see here, there are two type of post-processing treatment approaches has been found. One is sintering and one is chemical conversion.

In case of the sintering, the room temperature, it increases to 420 degree Celsius. Thereafter, it increases to 1100 degree Celsius and 1175 degree Celsius in case of full sintering. And then at the high temperature these materials were held or this inkjet or binder jet printed structures were held for 4 hours to 240 minutes and after that it is cooled. This is one kind of treatment. Another kind of treatment what we call chemical conversion.

It does not apply any heat but essentially it cures the materials or it converts the materials to a more stable phase. For example, we started with the salt, magnesium phosphate or ammonium hydrogen biophosphate, H_2O . essentially post harden this materials with 3.5 mole percent diammonium hydrogen phosphate solution, then you get this particular diammonium hydrogen phosphate solution and phosphoric acid. this particular X-ray diffraction plots, XRD plots which what is XRD that you know that X-ray beam.

they get diffracted from the planes of atoms and this X-ray beam when it gets diffracted from the planes of atoms what we have shown you earlier that how this there is a path difference $n\lambda$ is equal to $2d \sin \theta$ where d is the inter planar spacing and θ is the angle of diffraction. So it is the coherent interference and that is been used to analyze

the material structure and what you see here is that this particular case what we have seen that we are using magnesium phosphate. when you 3D print magnesium phosphate and you do PS printed and sintered, PC printed and chemically converted. when you have used that printed and sintered we get magnesium phosphate without any second phases. When you use printed and chemically converted you get farringtonite ($Mg_3(PO_4)_2$), ammonium, magnesium, phosphate this particular phase which is quite strong peak.

When you dope strontium with an amount $Mg_{2.5}Sr_{0.5}(PO_4)_2$ and $Mg_2Sr_1(PO_4)_2$, you get same struvite phase $NH_4Mg(PO_4)$, you get farringtonite phase and you get additionally phases which is marked as X which is $(Mg_2Sr(PO_4)_2)$ ($Mg_2Sr(PO_4)_2$) we get. essentially depending on the strontium, you get a range of phases which include struvite, which includes farringtonite and also include $(Mg_2Sr(PO_4)_2)$ We have utilized microcomputed tomography analysis and you can see this microcomputed tomography analysis gives you not only 2D ortho slices like the way I have shown but also they use the 3D volume rendered images. And 3D volume rendered images were essentially reconstructed from N number of 2D ortho slices and you can see different colour in the 3D volume rendered images and different colours essentially indicate the pores which are interconnected to each other and then how this interconnected porosity extends through the different parts of this 3D volume rendered images.

left hand side it is the post printed and sintered, right hand side it is printed and chemically converted. By looking at these two images and then inserts in individual cases is there is 2D orthoslices. By looking at these images you will agree with me. that micropore interconnectivity perhaps is much much better when these binder jet 3D printed structures were chemically converted in diammonium hydrogen phosphate solution. this is more on the quantitative analysis of the 3D microstructure and this quantitative analysis gives you pore size distribution, these pores and then you can see that equivalent pore diameter is kind of that is the mode you can see around 11.

5 micron. and this is much, much lesser. this is 16, this is 32, this is 48, it is kind of here somewhere around here. Whereas, in the equivalent pore diameters chemically converted materials, is around 9.63. this is the case for magnesium phosphate solution but this kind of porosity like 15% , 22% porosity that we have shown in this table it is for some of the strontium doped magnesium phosphate ceramic.

Like before we have also measured the mechanical properties of this 3D printed and post processed structures in both the two classes of materials like one is sintered materials and one is chemically hardened materials. We have used three mode of loading, one is that uniaxial compression, one is called flexural loading and third one is the diametral compression. whenever you see that I am describing the tensile strength of any ceramic

material, You must remember those tensile strengths are measured by the diametral compression configuration. traditional way of making the dog bone samples for metallic materials cannot be extended to ceramic materials because of their inherent brittleness. And particularly when you do binder jet 3D printing even the porous structures are much more fragile than even conventionally sintered 99.

9% dense ceramic materials. And like before We have also measured the strength properties on large number of samples to determine the viable modulus of this magnesium phosphate materials. So therefore one thing must be very clear to you that when one does research on the binder jet 3D printing of metallic materials or ceramic materials, one should not report the strength values of 2 or 3 samples or 3 or 5 samples but one must use large number of samples to show the reliable measure of the strength properties. reliable measure of the strength properties can only be assessed by measuring the wearable modulus that is the slope of the weakest link fracture statistics. just to revisit what I have mentioned to you that if you have a samples and the and the sample is essentially assumed to consist of N number of 1, 2, 3, 4, 5, so that N number of such volume elements and if each volume elements has porosity for example is one of the classical defects in binder jet 3D printing, 3D printed structures.

I would like to recapitulate here that the volume element which contains larger pore size which is of critical dimension or if these pores are favorably oriented towards this loading direction so that cracks can be very easily. originated from this pre-existing pores that can lead to the failure of this particular volume element, let us say volume element number 2 is broken or fractured. That can suddenly lead to the fracture of the entire samples I would like to remind you is the hypothesis behind this weakest link fracture statistics. And these simple mathematical equations which has been mentioned here, these are fundamental equations of the weakest-in-factor statistics where probability of failure of any sample is assigned as $n_i - 0$.

$5 / N$. In the first sample it will arbitrarily find out $1 - 0.5$ is the number of samples is 16 so that 0.5 by 16 is the probability of failure and you may well remember from the basic mathematics and statistics probability of any event must be less than 1 and if these two events are equally probable at any instance, their sum total must be equal to 1. that means whether a volume element survive or whether a volume element fail, if their survival probability is P_s and failure probability is P_f , their sum total must be equal to 1. And in this particular case, we have found out that what is the probability of failure of individual volume element.

And one can go through this hypothesis of Weibull weakest link fracture statistics which has been provided by Weibull, then you can come down to this, you can arrive at this

particular formulation which essentially shows probability of failure is 1 minus exponential negative of sigma by sigma 0 to the power m, what we call 2-parameter Weibull distribution where m is the Weibull modulus, sigma 0 is the characteristic strength. And if you take double logarithm of this equation and if you do some rearrangement then you can get to this particular double logarithm $\ln(1/P_f)$ is equal to $m \ln(\sigma/\sigma_0)$. Now, from this equation, it is of the form of y is equal to mx plus c. Now, if you plot $\ln(\ln(1/P_f)) / \ln(\sigma/\sigma_0)$, you should expect a straight line, the experimental results. And if you see this straight line, their slope essentially will give you the value of m.

that is viable modulus that is fairly straight forward and this m value has been mentioned consistently on the top of the plot corresponding to each of these data sets. And if you look at the blue one that is $Mg_2Sr_1(PO_4)_2$, the viable modulus is 8.8 close to 9. which is again a quite a good number as per the viable modulus of this kind of porous bioceramics are concerned. And if you look at this particular table, viable modulus of this brick, pottery and chalk is less than 3.

Engineered ceramics, remember this kind of engineered ceramics what I have mentioned is 5 to 10. They are viable modulus essentially reflect this is almost 100% dense ceramic and remember this particular ceramic has lot of porosity, even this kind of highly porous 3D printed ceramic structures you are getting the viable modulus of 8.8 that is quite a remarkable number that is what I trying to emphasize here. Some of the metals like you know aluminum and steel this has can go up to 90 to 100. Weibull modulus for ceramic materials or brittle materials is almost like one order of magnitude lower than that of the metallic materials.

in this one of the motivation for developing this strontium doped magnesium phosphate materials is essentially to see that whether the strontium can be released when these materials are placed in the physiological medium. there are a couple of tests or specific experiments which are conducted to find out that how strontium is dissolved in this particular in vitro medium. in vitro essentially means these experiments which are conducted using glassware. to simulate physiological context. What is physiological context? That means the body temperature is 37 degree Celsius, pH is 7.

4 and also it is phosphate ion and then this kind of salt concentration and other concentration which are maintained in a typical physiology body fluid those conditions were maintained and this particular binder jet 3D printing printed and chemically hardened materials were dissolved. And then what we have measured, we have measured the different ion release or adsorption of different ions and those are mentioned here what is the Mg^{2+} ions, what is the phosphate ions, what is strontium ions, calcium ions are

being released, what you can clearly notice In $Mg_2Sr_1(PO_4)_2$ the strontium release is more but it is certainly less than 0.25 milligram per gram compared to $Mg_{2.5}Sr_{0.5}(PO_4)_2$ higher amount of strontium in strontium-magnesium phosphate cement composition induces lower amount of magnesium and higher amount of phosphate release cumulatively.

in the summary the 3D binder jet printing with sintering and chemical conversion were demonstrated as a viable processing approach for strontium doped magnesium phosphate scaffolds and scaffold porosity as I mentioned that in particularly chemically converted structures It is very highly interconnected and pore size kind of varies kind of 8.4 or quite 10 to around 30 micrometer. Despite having lot of porosity, we have measured the Weibull modulus, the strength reliability is kind of 8.8 or 9 Weibull modulus that is quite good. And consistent release of strontium or phosphatins together will reduce release of magnesium ions that we have measured in chemically converted magnesium to strontium phosphate scaffolds.

This particular work was the result of the collaboration between Indian Institute of Science and University of Würzburg in Germany and this German student Susanne Meininger also visited Indian Institute of Science as part of this work and one of my former PhD student Saurabh Mondal also visited as an exchange visitor to University of Würzburg to complete this work and this work was published in ACTA Biomaterialia in the year 2016. Thank you and I will come back to you more lectures in line with the overall course content of this NPTEL course.