

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

Prof. Bikramjit Basu

Materials Research Center, Indian Institute of Science, Bangalore

Lecture 15

In the last lecture we have seen that how the in-situ polymerizable ink was used to binder jet 3D print the Ti6Al4V materials. We wanted to explore whether similar ink formulation can be equally effective for binder 3D printing of ceramic based materials. One of the ceramics that our research group has investigated in the past, and the ceramics I personally have investigated during my PhD thesis is the zirconia based ceramics. Consequently our aim was to see that for the zirconia can be 3D printed using that in situ polymerizable ink. What we have done? Initially we started with zirconia itself and then mixed with the initiator like the way we have done for the Ti6Al4V and then initiator concentration was varied, they were blended and then sieved and then 3D printed.

But we did not get appreciable strength properties and significant porosity in these materials we could not control or we could not reduce the porosity. Subsequently, we have developed a strategy to mix zirconia and zircon, that zircon is essentially zirconium silicate, it is $ZrSiO_4 \cdot 8H_2O$, this hydrated zirconium silicate and zirconia we have used 3 mol percent yttria stabilized zirconia. If we mix in 3 is to 1 ratio with the initiator, then we shift into 100-125 micron, then we use the 3D printing. So, what we have found out that in the core shell model printing that I have mentioned in one of the earlier lectures that is the typical characteristic of the binder jet 3D printing.

we have found out that we could print it, it has strength properties but strength properties is not very high and in this particular case we have used the binder as the TEMED added 22% acrylamide solution that you have seen in the last lectures also during the Ti6Al4V printing. Thereafter as the post binder jet 3D printing treatment, we have used strategies like infiltration strategies. And what is this infiltration? What is the binder that we have used at the binder jet 3D printing stage? Same binder we try to infiltrate into the 3D printed structure followed by sintering. Another approach we have used is the salt solution infiltration, zirconium silicate salt solution that we have infiltrated into the 3D printed structure and then it goes to full phase conversion during the sintering process. While doing the study on this zirconia is that powder bed packing that is very important and powder bed packing is strongly influenced by the powder characteristics, powder

particle size and other physical characteristics.

For example, in this particular case which is a very highly flowable powders. zirconia or zirconium silicate that somehow did not lead to good powder packing. However, if the powder is more cohesive because it should interact with themselves with the strong cohesive forces and binder alone cannot bind or trap these particles which are not packed cohesively. These kind of powders are much better the way I am showing with the laser pointer. Therefore, we selected the commercial sources which can provide us this kind of cohesive powder and we have utilized that in the binder jet 3D printing of this zirconia powder.

This is a little big slide. Let me go through slowly here. This bioceramics modification strategies, so first generation strategies is essentially the partial and controlled humidification for cohesive bed packing. What are the benefits? These powders are when it is partially moist, this core shell effect is minimal that we have found and some of the powder packs cohesively better than the unmodified powder. This shelf life is very less of the APS initiator and there is macro porous islands that what we have found.

Now, second generation modification is that metal silicate blending corresponding to the parent bioceramic chemistry like if you go back to this one zirconium silicate $ZrSiO_4 - 8H_2O$ is blended and there is no APS degradation and good cohesive bed packing that has been observed. Another approach is the dual deposition of powder to avoid macro porous layers and there we have found out the smooth layers without macro porous islands. If you go back to these basics of the binder jet powder printing, so for example this is the first layer deposition and this ink jet is continuously impacting on the powder bed. Then, printing status, powder sprinkling, then second layer of deposition it is initiated and second layer is deposited here powder sprinkling. Powder bed quality is very important in contributing to good properties of the 3D binder jet printed construct.

If we revisit the core shell methodology, so core essentially region where there is a lower saturation. And shell is the region where is the higher saturation. It is very characteristic of the conventional binder jet 3D printing process. And the core shell printing, so saturation essentially is that what is the volume of ink that is required in reality to the ideal condition that ratio is the saturation. And this is a drop and demand approach that we have been discussing for last few lectures and this is the 3D binder jet printing with acrylic binder that I would like to remind you.

With this machine default core shell printing one has to bypass, otherwise what we found that there is no way you can improve. the quality of the as printed constructs, the properties of the as printed constructs particularly in case of the zirconia. And you can

see that large number of cylindrical and rectangular cross-section samples were binderjet 3D printed and also sintered and thereafter they were essentially fractured under either the compression like cylindrical cross-section samples were fractured under compression, whereas rectangular cross-section samples were fractured under 3-point bending configuration. And you can see that how these cracks are originated from the tensile phase that is the opposite to the loading phase and from the tensile phase cracks generate and then they propagate leading to the failure you can this is again a busy slide with lot of experimental results. therefore, let me spend some time to explain you.

this is the X-ray diffraction. left one this is that X-ray diffraction results that you remember that I have mentioned $n \lambda$ is equal to $2d \sin \theta$. that is the Bragg's law that is followed in this X-ray diffraction and what you see here is that intensity versus 2θ plot. you can see certainly this 3D printed construct contains crystalline phases because it has a very sharp peak that is number 1 observation. Number 2 observation, depending on the peak positions, you can identify an intensity of the peaks, you can identify what are the phases that are present and zirconia, they have 3 polymorphs.

One is a tetragonal symmetry, one is a monoclinic symmetry, one is a cubic symmetry. In tetragonal zirconia has a characteristic this 3 peaks here. you can see some of the tetragonal peaks and there is also two monoclinic peaks in 2 sides. the strongest peak is tetragonal, two sides is the monoclinic peak. Zirconium silicate or zircon sand that we have used.

that we have mixed with the zirconia during the 3D binder jet printing and or in the powder bed itself that is certainly remained there even after sintering at 1450 degree Celsius. As I have mentioned that in some of the cases we have used some salt like zirconium oxychloride and when we use zirconium oxychloride you get more full conversion of the tetragonal zirconia. You do not see any other phases except tetragonal zirconia and also monoclinic zirconia is not there. no monoclinic zirconia that is important. Because if you have monoclinic zirconia that essentially compromises the strength properties, hardness properties, toughness properties of zirconia.

In order to have good zirconia product, one should always remember that you must have as less as possible monoclinic zirconia and as high as tetragonal zirconia particularly in 2 to 3 mol percent or 4 mol or 2 to 3 mol percent yttria stabilized zirconia products. Whenever we are handling with tetragonal zirconia polycrystals, our aim is to retain 100% tetragonal zirconia in the final as processed samples. As you can see 3 mole per cent yttria stabilis zirconia at 1450 degree Celsius, it is pure tetragonal phase. It is a strong phase and there is no deviation in the or there is no peak shifting. The peak shifting things also I have mentioned when I have discussed about the characterization

techniques of the materials characterization.

This is the compression tests and you can see this large cracks that has formed and goes through the perpendicular directions along the loading directions and this we have not only done this is the cylindrical samples but this is something called diametral compression test. Diametral compression test essentially means you get the D shaped samples and these samples you put it on the compression. So essentially you test the D shaped samples and then apply the compression force. If you know more about the mechanics of materials then you will be able to realize that although actual compression load is being used but D shaped samples essentially will experience primarily the tensile stress field. This is one of the ways for ceramic materials one can measure tensile strength because you take the diametral compression samples, you put them under compression and essentially you measure the tensile strength.

And the reliability of the test results has to be validated by showing these kind of observations or evidences where you can clearly see the diametral compression test cracks propagate along the diameter. suppose in the diametral compression strength crack propagates randomly like the way I am drawing, this is not good. These kind of evidences if you see after the fracture is over, then certainly it should be clear that this will not give you reliable tensile strength from the diametral compression strength. ideal evidences is like along the diameter the crack propagation. what is the tensile strength you are measuring? It is very low.

It is 1 MPa because it is a highly porous structures. Compression strength, it is around 7 megapascal and flexural strength is around 12 megapascal for n greater than 16. that is more than 16 samples were used for these measurements. As I mentioned and then you would also realize by now this 3D binder jet printed zirconia also have lot of porosity. this kind of porous binder jet 3D printed structure should also behave in a more like a brittle manner in this particular case.

What I was discussing that binder jet 3D printed zirconia ceramic was equally porous like the binder jet 3D printed Ti6Al4V Therefore, the reliability in measuring the mechanical properties was emphasized. and therefore that we have printed large number of samples and those large number of samples were tested under different loading configurations whether compression or flexure or diametral compression tests. And then when we have used weakest link fracture statistics as I have explained to you in the last lecture in the context of binder jet 3D printing of Ti6Al4V, we have found that Weibull modulus that one can get for this binder jet 3D printed zirconia is not bad, it is 9.6. Actually it is a relatively good Weibull modulus considering very porous zirconia ceramic.

However, their mean strength is fairly low around 12.2 megapascal. We consistently use this stochastic fracture statistics for any of the 3D printed structures whether it is a metallic samples or ceramic samples primarily because of the fact that it has good amount of porosity in the 3D printed structure. what is the message that has been mentioned in the center of this slide is the total binder formulation that you mix the initiator with the powder and then you use the monomer solution together with the accelerator dissolved in the deionized water. and allow this in-situ polymerization to take place during the binder jet 3D printing.

This approach was also efficient in 3D binder jet printing of bioceramic materials. However, mechanical properties remain inferior and that is due to the machine limited core shell kind of printing. We need to go away from this default setting, default machine dimension by strategically modifying the powder or the CAD files. what I am trying to tell you is that there are two approaches or there are two ways you can avoid this. One is the powder based approaches.

And another one is the modification of your CAD files which you prepare using the Solidworks . The powder-based modification processes you might realize that I have discussed in few slides back that there can be two approaches in the powder-based modifications. One is the infiltration of same binder solution. or salt solution, that salt solution as I mentioned to you during the zirconium oxychloride. Now, when you infiltrate zirconium oxychloride solution into the 3D printed construct and after that you sintered them, essentially you allow zirconium oxychloride based solution to be converted to zirconia.

you get the same zirconia but using a precursor salt solution. these are like two approaches that one can get in the binder jet 3D printing particularly when drying with this zirconia based materials. let me just show you that what are the approaches that we have used. first thing is that if you use the unstabilized zirconia like 0 mole % Zirconia, if you infiltrate into the zirconia powder bed, then that we have seen that that causes failure. We have prepared a small experimental setup.

you can see this is the binder jet 3D printed structure, this is the 3D printed sample. So, you essentially evacuate the microbial parts of sintered scaffolds and after that you put it there, then you actually add this that infiltration of saturated $ZrOCl_2$ solution into it, then emerge it for you do the infiltration treatment after the drying and then sintered it for the zirconia conversion. you have the as binder jet 3D printed particles and this is your partially sintered particles. And after this what you expect? You expect that this is the region through this capillarity region zirconium oxychloride is essentially infiltrated

right. zirconium oxychloride solution is essentially infiltrated into this capillary.

Then after you dry you heat treat at 450 degree Celsius and then dry it and when you sintered after the drying you sintered and then you get converted tetragonal zirconia. And then if you sintered then essentially many times we see that you know it can transform to monoclinic zirconia volume expansion and crack formation. infiltrated zirconia needs to be stabilized to avoid any monoclinic zirconia phase transformation that is what we learnt when we strategize this particular zirconia infiltration. this is like you know 4 random functional parts were infiltrated and converted and then we can also find out there is a considerable weight gain after first conversion, second conversion, third conversion and so on. what I am saying this infiltration process needs to be repeated and so that you know it is stabilized, it actually gets infiltrated into all the available capillary pore spaces and capillaries before you do that.

this work was published in Open Ceramics, that is the European Ceramics Society journals. And again, this is a work from, this is the first author is Srimanta Barui during his PhD thesis. Now, let us move on to the second approach. first approach is essentially the materials based approach, second approach is more on the modification of the CAD design. what you see here in the top panel essentially shows a rectangular architecture and bottom panel essentially shows the cylindrical architecture.

In the top panel, in the rectangular architecture, you can do the 3-dimensional structure essentially which is composed of a plurality of 2-dimensional layers. Each layer of the plurality layers comprise the plurality of segments formed by providing one or more slits. These are like slits you can see in each of the 2-dimensional layer. Now, in the core shell mode of printing, you have a core.

and then you have a shell right. what we did actually if you consider the C-D layer here it is the place where inter segment bleeding of this binder takes place and there is a E-F layer that is the also the region of the inter segment bleeding the binders. We discretized and segmented the printing and that leads to the highest saturation, of the binder without any core shell effect as has been mentioned here. This has been clearly shown this particular area if the lower saturation then if you go to region here is the higher saturation and binder bleeding and joining is much more effective. this aspect is very well proven in our study. you can see that we have taken these photographs during the binder jet 3D printing.

You can see zirconia based materials where these zirconia based materials were getting printed. It is the initial stage. It is almost at the final stage and then segmented CAD model essentially was used to remove the core shell mode of printing. this is segmented

core, this is unsegmented CAD essentially causes the core shell. After that we have used the dual deposition technique in enhancing the packing powder bed quality and packing density.

if you see that weight measurement of the trapped powder and then surrounding powder bed method when you do this powder bed tapping of the as deposited and we have done this weight measuring of this known things, then we found out that powder bed density without dual deposition was little less, it was like 1.5 and then it increases to 1.8 with dual deposition. what we have used is the modified infiltration method. In the modified infiltration method, we use $ZrOCl_2 \cdot 8H_2O$ together with $Y(NO_3)_3 \cdot 6H_2O$

this is the precursor solution. in a vacuum when we infiltrate in drop by drop method in the pre-sintered green bodies, this is pre-sintered green bodies means it can be also 3D binder jet printed materials. right. this is the step 1. In the step 2, we actually add this ammonia in a drop wise manner. Then step 3, you convert them at 600 degree Celsius to yttria stabilized zirconia so that yttrium is also fused to the zirconium particles and if you repeat that step 1.

step 2 and step 3 these things couple of times then you stabilise the zirconia and then finally you do sintering at 1400 degree Celsius for 5 hours. This is in contrast to what you have seen in the last lecture is that one can use the infiltration of the zirconium oxychloride solution itself and this zirconium oxychloride $8H_2O$ solution will not give you stabilized zirconia but it will give you more pure zirconia and whenever the zirconia particles are unstabilized this will certainly form monoclinic zirconia after the sintering process is over. this is what it has happened in this particular case and then what we can see that after this multiple iterations of the step 1 to step 3, we are able to get sintered zirconia and you can very clearly see that you know t-Z is essentially tetragonal zirconia, M-Z is monoclinic zirconia and you can see that S1 and S2 essentially 2 random samples to endorse consistency in phase assemblage. density wise it is fairly low it is close to 3 and zirconia density as you know it is 6.1 gram per cc so it is much lower than that is almost like 50% of that porosity.

One of the clear evidences what we have got from the segmentation or the removing core shell is that this is the unsegmented core. You can see here is highly porous core region. Now, when you have this segmented core, you do see microporosity, which I have repeatedly mentioned that you cannot avoid in case of this. This is a microporous region.

in case of the binder jet 3D printed structure. But we do not see any gradient in porosity certainly not like that. This is what it is not desirable. This is still in the acceptable range of the microstructure that one would expect in the binder jet 3D printed structure. I am

not going into more details but similar methodology was used to measure the flexural strength and compressive strength and what you can see here in the un-segmented core region, the flexural strength was 10 megapascal, it increases up to 12 or 12.5 or something compression strength is increased much more significantly.

It was like 4 megapascal it has gone up to 14 megapascal more than 3 times the compression strength after the CAD file based modifications were done. what you can see there is a CAD file based modifications there is also modification the infiltration stage both of which synergistically impact and to improve the strength properties of the zirconia. Now, what about this viable modulus or strength reliability? we have done sufficient number of samples, we have loaded in flexure and we have loaded it also in under uniaxial compression. in case of the core shell things, you can see viable modulus is around 3.

2, it increases to segmented core is like 3.8 that is the viable modulus. segmented core and core shell architecture. In case of the compression strength, Weibull modulus was initially 6 and that it increases to 6.3. one side it is failure probability, another side it is the $\ln[\ln\{1/(1-p_f)\}]$ we actually you know that we try to see you know how this can be used for making some of the complex structure, let us say femoral stem.

We still have to go further for that just to see that how the large structure can be binder jet printed. This was published in Journal of European Ceramic Society as part of the PhD thesis of Srimanta Barui in IISC. I will come back to you on more scientific case studies in the next lecture.