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

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Lecture 13

In continuation with the scientific case studies related to the 3D printing, I shall discuss the biometric 3D printing of Ti6Al4V using in-situ polymerizable ink. In the last lecture I have covered the binder jet 3D printing of the same material with starch based printer and I have shown how one can do 3D binder jet printing for uniform porosity for Ti6Al4V with uniform porosity and gradient porosity. and subsequently I have shown that how one should correctly use the micro CT image of the 3D printed scaffold as an input to finite element analysis and also to find out that how the mechanical properties which are experimentally measured correlate with the computational biomechanically analyzed results. paramount significance in various engineering applications, our research group has conducted considerable work on the Ti6Al4V not only using binder jet printing but also using selected laser melting and directed energy deposition, all the three variants of these 3D printing techniques. Let us revisit the. 3D inkjet powder printing or 3D binder jet printing or the overview of the 3D binder jet printing.

Remember one thing that in typically ISO literature this particular technique always referred to as binder jet 3D printing. However, in scientific literature you will find that it is mentioned as 3D inkjet printing or 3D inkjet powder printing all are synonymous. So, what we learnt in the last lecture when I have put I have made an overview of the 3D binder jet printing that it is a drop on demand. Drop on demand means that each time the binder is ejected from the print head.

impacting on the powder bed and subsequently infiltrated into the powder bed depends on the information contained in the design file. And, according to the instructions provided in the design file that each time from the feed bed to the build bed each layer of the powder will be displaced and then this binder impact and infiltration will be synchronized with the layer displacement from the feed bed to powder bed. And therefore, several parameters are of importance which include layer thickness, printing speed, binder saturation. And in terms of that binder properties which are of relevance that is viscosity, surface tension and density. Most of the things I have explained but I thought that I will revisit these basic fundamentals and so that I can continue with the more scientific case study.

What was the concept behind this set of experiments? This is that binder development or binder formulation is one of the key thing in the binder jet 3D printing. Any new technology for materials using binder jet 3D printing often includes new binder development and this binder development that whatever I am going to show you and whatever I have shown you earlier this binder formulation is already patented and has been granted Indian patent as well. This is the powder to be printed. This is the Ti6Al4V powder, What we have done, this is the work from Srimanta Barui, one of the former PhD student. We have essentially mixed with the initiator.

This initiator is either APS/KPS 4 to 8 percent. Then this particular mixture is put it into the ball mill where 3 is to 1 ball to powder ratio is kept and then this is like a standard ball mill. In terms of the binder formulation what we have done we have used monomer that is acrylamide and accelerator that is TEMED that is 1 to 3 percent. And this monomer and accelerator is mixed with deionized water and that forms the monomer solution. what happens this monomer solution is now injected into the powder layer on the built bed.

And, this is that from the feed bed to the build bed. That each time the printer head actually displaces from the feed bed to build bed, this binder impacting and infiltration is synchronized. And then when this physical interaction takes place and when the binder is ejected and this is the binder path. When it is ejected from the inject nozzle that we have put some high speed camera. And this high speed camera essentially allows us to take the shadow graphs and from the shadow graphs one can find out that what is the binder particle diameter or binder droplet diameter that is being ejected and which is interacting with this kind of powder bed.

what was the idea behind this particular binder formulation? what we hypothesized is that once this binder comes, it will impact, so it can flatten on the powder bed. And once it is flattened, it is very easy that it can be infiltrated into the powder bed. And during this binder injecting since we are using this monomer solution we believe that it will undergo in-situ polymerization and this concept of in-situ polymerization also we have analyzed using DWS. So, when capillary infiltration takes place, when the binder infiltrates into the powder bed, we have also quantified that what is the time of infiltration and what is the wetting contour using Washburn model. Now, why this binder will infiltrate and why these binder properties are useful for 3D inkjet printing? As we have mentioned in one of the earlier lectures, there are certain dimensionless numbers from the fluid dynamics which are useful and these include Reynolds number, Weber number or Ohnesorge number.

We were able to determine those dimensionless numbers based on the binder droplet diameter. This was essentially the shadowgraphy technique was used and that was very helpful to quantitatively analyzed the physics of the binder materials interactions. This is essentially a video what you can see that when this particular high speed camera is focused as the binder droplets is ejected from the inkjet nozzle and this particularly these shadow graphs were taken at 20000 frames per second very high speed camera and that was used further to find out that what is the droplet diameter distribution and if you see this diameter is around 50 micron. It is more like a log normal type of extended tail type of distribution okay. This particular data were subsequently used to find out that what is the Ohnesorge search number, what is Reynolds number and what is Weber number.

here different parameters are mentioned, A is your nozzle diameter, rho is your density, gamma is your surface tension and v is the velocity and eta is the viscosity. from this we can find out instead of this is the nozzle diameter, this is essentially droplet diameter. from this you can find out that what are the different dimensionless number and based on this dimensionless number essentially we can find out that if you plot one ohnesorge number along the Y axis and Reynolds number at the X axis. The binder that we have used here that falls well within this green shaded region that means it essentially falls in the printable fluid region. And that is the reason that we are able to print these materials fairly easily and in a reproducible manner.

And then if you look at the deionized water and the novel binder this comparison you can see the Reynolds number for deionized water is 6.25. Here in the inner binder it is 5.2 slightly less whereas Ohnesorge number is quite high. Because typically deionized water if you look at this falls under here.

this is the insufficient energy for drop formation this region. But the binder that I have described in last few minutes their properties or the dimensionless number of that specific binder allows that binder to fall in this printable fluid region. Essentially what we have done we developed more understanding to find out that how the dynamic viscosity of this particular binder that varies with the angular frequency or shear rate and we have found out that in case of frequency sweep it shows a decrease and thereafter very steady state value of around 20 millipascal second. In case of the static viscosity with shear rate, this also shows some decrease but it is essentially more or less constant at 1 millipascal second. This viscosity, surface tension and droplet velocity, droplet diameter, these were actually very important measurement that we have carried out.

Next one that we are going to cover, so first I have shown you this ink flight and then all this dimensionless number. Next one I am going to show you how we have quantitatively determined the capillary infiltration using Washburn model. Phenomenologically what happens that your binder droplet comes and this binder droplet essentially interacts with the powder bed. It will flatten and then it will penetrate into the available pore spaces in the powder bed. And what I have shown you here, it is the ideal packing of spherical particles.

We consider the titanium 6, aluminum 4, vanadium powders have each having spherical particles and if these spherical particles are packed together, then there must be some available spaces and these available spaces are the spaces through that will be transport path for these binders to be infiltrated into the powder bed. We have done very simple pen pencil type of calculations and then find out that what is the typical depth, what is the path distance and so on. And this is the kind of you know this is one plane mm and plane nn and then we are trying to find out that what is the path that this binder actually traverses each time it infiltrates into the powder bed. from simple geometrical considerations if you look at that the vertical distance between plane M and plane N is essentially LV and if you consider AB, so it comes out to be 2 plus AB tan 60 into R, R is your particle size, right. it comes from this expression is 3.

73 r. And then cumulative length of arc AD that is that arc AD and cumulative length of arc AE and then also arc EF and then arc FG. So essentially this path the way I have been traversing, so let me continue with this. basic mathematical framework that we have used based on the simply geometric considerations. What I mentioned that suppose these two, this plane MM and plane MN essentially the two vertical planes and in between these two planes these 5 powder particles spherical sized uniform sized powder particles are contained. what is the distance between these two planes? It is 3.

73 times r, r is your particle size. Now, if we consider this arc length of AD and AE, then arc length AD, AE, EF and FG then that will essentially show you the tortuous path that binder will travel during that capillary infiltration process. And this tortuous length of the inkjet travels in real space is 1.

05 r plus 1.57 r, so 2.62 r that would be multiplied by 2 because since it is a uniform particle size, so this particular arc length and this particular arc length, their summation would be same as this particular arc length and this particular arc length. That gives rise to 5.24. What is the tortuous path to the distance between two plants, that ratio comes out to be 1.

41 or square root of 2. what we have used, we have used that Washburn model and this Washburn model allows us to find out that what is the time for capillary infiltration of the

ink. what are the different physical parameters or physical properties of relevance that is viscosity and density, that is the capillary pressure, dynamic contact angle. effective capillary radius and tortuous capillary length. These are the different parameters which we also have calculated based from geometric considerations. And if you do that and then if you essentially modify the Washburn model which has a large equations and then different parameters are already mentioned here.

That will allow us to give what is the time of infiltration and this time of infiltration is very important, this is the t, t is your time of infiltration is very important, lT is your capillary length, r is your particle radius, rho is your density. g is acceleration due to gravity, eta is viscosity. these are all different parameters that I have mentioned here. that gives rise to what is the time of infiltration. we have also done synchrotron validation and in situ monitoring under the synchrotron beam line and then we can find out that what is the ink infiltration into the powder bed.

What is the Washburn capillary rise model? That can be used for dynamic contact angle measurement. Originated from this particular Poiseuille's law, the simplified Washburn equation L square by T is equal to R gamma cos theta by 2 eta. here consider the cylindrical capillary mass of a liquid with density rho content M is equal to rho V where V is pi R square L and M is pi R square L into rho. if you do simple substitutions to this first equations then you get M square by T is nothing but CB. Cb rho L square gamma divided by eta cos theta.

What is Cb? Cb is your bed constant and capillary diameter capital D is 2r. this is the schematic that has been shown that you support and test liquid is essentially travelling upward directions through this powder bed. we are trying to find out that you know that how this capillary infiltration takes place and what is the time scale of such infiltration. Original paper of Washburn was published in Physical Review more than 100 years ago in 1921. we use this particular theory, to find out that what is the, how this Washburn's model can be utilized in our case.

what it shows what these 2 plot essentially show that when contact angle is 0 degree like in a hexane medium this powder bed this slope of this particular part the linear part when weight square is essentially plotted as a function of time. it is m square this mass square as plotted as a function of time. it should give you typical value of 0.05 gram square per second. if you change this medium from hexane to acrylic ink as is the case in the present Ti6Al4V binder jet 3D printing, we obtain contact angle is 43 degree.

And from that if you plot M square here and this is the function of T then you get the similar slope here the linear part is 0.0034 gram square per second and from their bed constant powder bed related constant CB value is 1.5 cent 10-15 meter cube. this essentially analysis was also followed in this experimental validation of ink filtration under synchrotron BEM line. this is like you know overall quantitative understanding of the process dynamics.

what you see this is the plot for the M square versus T and this is our ink, this is the reference that is the hexane solution. And this is what we call Karman's model of tortuous path. I repeat what we have done, we have calculated the arc length of AD plus AE plus EF plus FG. So, that is the tortuous path that we have found out. We have also calculated from the simple geometry that what is the distance between these 2 planes and from that we find out this is the LV and this is that what is the tortuous path So that calculations we have done earlier and then we have shown and then we have found out that what is the CB value bed constant.

there is a technique called diffusing wave spectroscopy technique. This technique is very commonly used by many physicists. it is very well-known technique in the physics domain which was also used to find out that what is the in-situ polymerization, how to establish the theory of in-situ polymerization using diffusing wave spectroscopy. this was used and then how this entire thing works. a laser beam which passes through a lens is focused on a particular gel type viscous medium, viscous polymer which has tracer particles.

And these tracer particles are specifically used for you know in this particular diffusing wave spectroscopy very commonly to trace the photon random walk then when this laser beam will incident or interact with this particular viscous liquid. And this diffusing wave is generated and then that will form the speckle at the CCD camera. you get the intensity versus time this kind of plots and those intensity and there are also there are other analytical results that you get which are extremely useful to find out what is the diffusivity of this particular medium and how the diffusivity essentially are related to the time of reactions. if you go back to this earlier in-situ polymerization formulation like if you remember that you know that one that there are important constituent in this particular case is that powder is mixed with APS. and then APS can be varied between 4 to 8% and monomer concentration, monomer is acrylamide and your accelerator is also varied in 1 to 3%.

what we are trying to probe is that how this initiator variation will trigger the in situ polymerization reactions. essentially this diffusing wave spectroscopy technique what we are essentially showing you that If you vary that APS concentration from 0.2 molar to 0.8 molar that how the diffusivity changes with time and we have used the linear fit of the experimental data. Experimental data is this one, the board line and dotted line is a linear fit.

And we find out that what is the diffusivity which is somewhere around between 10 to the power minus 6 and 10 to the power minus 4 micrometer square per second. it is very very low and what is the relaxation time in second that is also in millisecond 10-3 to 10-1 at that level and it is also dependent on the what is the APS concentration. data were validated that how G2t-1 will evolve with time and this particular case you can see that 0.4 molar APS solution that how it is varying from 40 seconds to 360 seconds. that actually shows the validation of the diffusing wave spectroscopy results in this specific case.

I repeat this is physics based measurements which were used to quantitatively analyzed the polymerization kinetics that is happening at the binder jet. powder interaction front, the two things that we have found out from here, one is the D value that is the diffusivity constant and how it varies with the time of reactions and remember the time of reactions is always in the second and what is the relaxation time or this particular characteristic time constant that we have used in this particular time of reactions. I will come back to you with more discussion on this in-situ polymerization and this particular binder jet 3D printing. Thank you.